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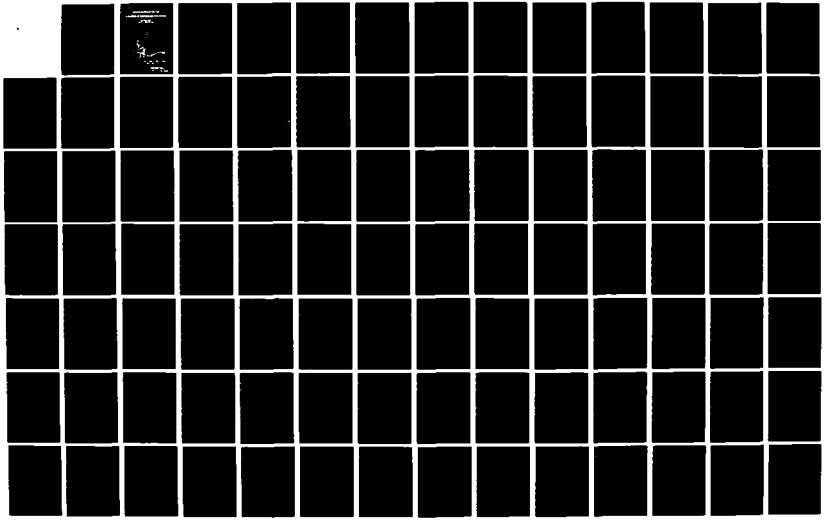

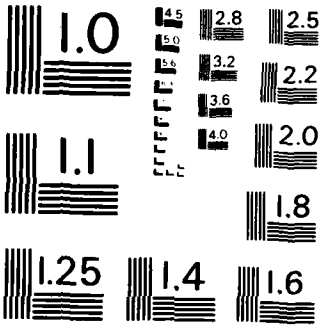

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The 1985 Conference on the Dynamics of Molecular Collisions was held at Snowbird, Utah on July 14-19, 1985. It was attended by 280 scientists, and there were 25 plenary lectures and 180 poster papers. The conference organizers were D. G. Truhlar, chairman, and P. J. Dagdigian, vice chairman. The research discussed at the conference included reactive scattering studies with state selection and aligned reactants; reactive and nonreactive resonances; reactions of transition metal ions; reactive close coupling calculations and the distorted wave and quantal transition state theories of reactive scattering; potential energy surfaces; experimental studies of vibrational and rotational energy transfer collisions in the vapor and condensed phases, in ions in flow tubes, and at surfaces; collision-free energy transfer; infrared and visible fluorescence, theory and experiment for collisions of open-shell and

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electronically excited molecules; collisional interactions of molecules with surfaces; desorption; helium beam diffraction; and photodissociation. The plenary discussions following the lectures were exceptionally vital and provided a strong indication of the current excitement in this field. The posters covered an even broader spectrum of work on the dynamics of molecular collisions.

to be published in Comments in Atomic and Molecular Physics

The 1985 Conference on the Dynamics of Molecular Collisions

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The 1985 Conference on the Dynamics of Molecular Collisions was held at Snowbird, Utah on July 14-19, 1985. It was attended by 280 scientists, and there were 25 plenary lectures and 180 poster papers. The conference organizers were D. G. Truhlar, chairman, and P. J. Dagdigian, vice chairman. In this report we highlight a selected subset of the research discussed at the conference. For invited speakers affiliations are indicated in parentheses.

As reviewed by J. Valentini (University of California, Irvine), there is increasing interest in reactive scattering studies with initial or final state selection. Examples of the former include studies of the reactions $Ca + HF(v=1)$, $Ca(^2P^o_J) + Cl_2$, and $Xe(^3P_{0,2}) + IBr$. In the first, vibrationally excited HF was prepared by Zare and coworkers by irradiation of HF with an optical parametric oscillator; such a tunable infrared source is much more versatile than the line tunable chemical lasers previously employed in such studies and allowed investigation of the dependence of reactivity upon rotational state. Optical pumping state selection with a cw dye laser was utilized by Dagdigian and coworkers in the reaction of metastable calcium for the study of reactions of individual spin-orbit states; significant differences in reactivity were observed in spite of the small energy differences between the levels. Martin and collaborators prepared aligned IBr reactants by taking advantage of the dependence of the photodissociation cross section on alignment angle.

Several examples were also given which illustrate the level of detail presently attainable for product state distributions. State distributions of HD produced by the $H + D_2$ reaction, which is of fundamental interest in chemical kinetics, have been measured by coherent anti-Stokes Raman scattering (CARS) by Gerrity and Valentini and by multi-photon ionization (MPI) by Zare and coworkers. Their results are in reasonable agreement with each other

and with a quasiclassical trajectory study by Blais and Truhlar. The CARS and MPI detection techniques are complementary in that MPI has high sensitivity but difficulties with respect to calibration, while CARS is generally much less sensitive, but it is more straightforward (although tedious) to reduce a CARS signal to populations.

A high-resolution crossed beam experiment in the laboratory of Lee on the $F + H_2$ reaction has revealed drastically different angular distributions in the product HF as a function of vibrational state. This has been attributed to resonances in the reactive scattering process; this is the first time such features have been identified experimentally.

J. Beauchamp (Caltech) showed results indicating that the reactions of transition metal ions with hydrocarbons exhibit a wide range of reactivity. The differing reaction pathways, e.g. C-H vs. C-C bond cleavage, can be correlated with the electronic configuration of the ion. J. J. Sloan (National Research Council of Canada, Ottawa) described the implementation of time-resolved Fourier transform infrared emission spectroscopy for the measurement of product vibrational distributions. This method is most conveniently employed in conjunction with photolytic preparation of a reactant. An example of the utility of this technique was given by the $O(^1D) + H_2$ reaction, for which it was possible to observe OH products in the v=1 to 4 vibrational levels. By contrast, laser fluorescence detection, while more sensitive, is limited by predissociation essentially to the v=0 and 1 levels.

W. H. Miller (University of California, Berkeley) presented an overview of the theory of reactive scattering. He pointed out that 28 of the 52 theoretical posters on reactive scattering were based on classical trajectories, which he characterized (in a favorable way) as "mindless". Considerable informal discussion during the rest of the meeting confirmed that indeed "mindless" theory is what we all want, provided it explains experimental results "properly".

Unfortunately, as also pointed out by Miller, trajectory studies do not fill the bill for many problems since they do not explain, e.g., resonance structure in the energy dependence of cross sections or other interference effects in product distributions, or threshold behavior of cross sections or tunneling. Miller emphasized recent progress in using the multichannel distorted wave approximation to calculate reaction cross sections in threshold regions, he reviewed the reasons why reactive scattering formalisms based on exchange kernels are very promising for supercomputer calculations, and he presented a tentative new quantal transition state theory, based on integrating a flux-flux time correlation function up to its first zero.

G. C. Schatz (Northwestern University) presented new quantal scattering results for several reactions, indicating that, thanks in part to the supercomputer revolution, the long dry spell in producing converged reactive cross sections for systems other than $H + H_2$ has now ended. John Murrell (University of Sussex) reviewed aspects of the many-body expansion for representing potential energy functions. A particularly appealing feature is the use of the integrity basis for generating fitting functions.

R. J. Gordon (Univeristy of Illinios, Chicago) reviewed recent experimental progress in a number of areas of energy transfer research. Quite a few studies, including recent work of Weitz and coworkers, indicate that it is often possible to extrapolate vibrational relaxation rates from gases into condensed phases by the independent binary collision model; now, however, Weitz and coworkers have found a case where this model fails. For larger molecules, detailed state-to-state measurements by Lawrance, Knight, Steinfeld, Kinsey, Field, Gentry, Giese, Fahr, Bates, Gordon, and coworkers in the gas phase have shown that specific vibrational modes are excited most favorably in both excitation and de-excitation collisions. Two groups have employed uv hydride photolysis to study collisional relaxation processes involving fast H atoms. Gordon also presented new measurements based on the shape of an acoustic wave vs. time after a laser pulse indicating that vibrational-transitional relaxation of highly excited SF_6 in

argon is much slower than might be expected for such a large molecule.

In a session devoted to collisional and collision-free energy transfer, J. D. McDonald (University of Illinois, Urbana) presented infrared fluorescence spectra from molecules excited with an optical parametric oscillator to single vibrational, and in some cases rovibrational, levels. Collisionless energy flow was inferred from the fact that the total emission rate was less than that predicted by the absorption oscillator strength, as well as by the presence and variation in intensity of many bands in the fluorescence spectra. The dilution factor of the oscillator strength was found to increase as the density of states increased but was too large to be accounted for purely from the density of vibrational states. Observed differences in the emission spectrum from single rovibrational states indicate the importance of Coriolis effects in this collisionless relaxation process.

C. S. Parmenter (Indiana University) made connections between collisional and collisionless relaxation processes, using the example of p-difluorobenzene. For low to moderate energies, collisional propensities are observed in the state-to-state collisional rates, with the most important mode being an out-of-plane mode. At higher energies, this mode also promotes collisionless relaxation.

A. E. W. Knight (Griffith University) addressed the question of whether vibrational relaxation is greatly enhanced by very low kinetic energy collisions. His first point was that the vibrational relaxation rate k_V should not be compared with a hard-sphere collision frequency, but rather with a Lennard-Jones rate k_{LJ}, because of the importance of the attractive interaction at low energies. Experimental results for the relaxation in electronically excited benzene and naphthalene by argon were presented. A free-jet expansion was employed and the fluorescence spectrum upon laser excitation of single vibrational levels was observed as a function of the distance down-

stream of the nozzle. Only a slight enhancement of the ratio k_V/k_{LJ} was found as the mean relative collision energy dropped from 20 to 2 cm^{-1}, while the absolute rates increased by a factor of about 4.

A talk by P. Andresen (Göttingen) exemplified the increasing interest in collisions involving open-shell molecules. He presented measurements of state-to-state rotationally inelastic cross sections involving two $^2\Pi$ molecules, NO and OH. A particularly interesting aspect of such molecules concerns the role of the closely spaced Λ-doublet levels. Since the incident molecules in these experiments have an equal population in the doublets of the lowest rotational level and case (a) coupling is rather good here, no Λ-doublet preference is seen in the final NO states, in agreement with the propensity rules elucidated by Alexander. By contrast, unequal final Λ-doublet populations are observed in OH because the coupling is intermediate between cases (a) and (b). This collisional propensity and similar effects in the VUV photodissociation of H_2O can explain the pumping mechanisms for most OH astronomical masers. Previous mechanisms relied on an erroneous assignment of the Λ-doublets.

In a comprehensive review of ion collisional processes, E. E. Ferguson (NOAA, Boulder) illustrated how the vibrational state dependence of charge transfer could be utilized to study vibrational relaxation of molecular ions.

D. C. Clary (Cambridge University) reviewed the current status of inelastic scattering theory. He singled out for special attention the poster paper of Keil and Parker in which 9 dynamical properties were fit by a single empirical He-CO_2 interaction potential and the poster paper of Schaefer and Monchick based on accurate potentials for HD - H_2 and HD - He. Usually though the interaction potential is much less certain. Other recent work on rotational energy transfer has involved rainbow and resonance effects. For vibrational energy transfer, recent progress has been made with the combination of vibrational close coupling and an infinite-order sudden treatment

of rotation. Clary challenged the experimentalists by predicting narrower vibrational predissociation linewidths than they have observed, but Bowman commented that lack of full rotational coupling in Clary's calculations may artifically narrow his predicted resonance widths.

M. Alexander (University of Maryland) showed how propensity rules in collision-induced rotational and fine-structure levels in open-shell molecules can be understood in terms of a spin-free tensor opacity. Alexander's formulation of the collision theory of open-shell molecules in terms of spin-free tensor opacities allows semiclassical trajectory claculations to be used to calculate fine-structure transition probabilities. G. D. Billing (University of Copenhagen) showed how semiclassical calculations have advanced our understanding of vibrational/rotational energy transfer collisions of small closed-shell molecules, including He - NH_3, Ar - CO_2, HF - HF, Ar - SF_6, and He - CH_3OH.

In a review of recent experiments on the interaction of molecules with surfaces, R. N. Zare (Stanford) focussed attention on measurements of internal state distributions of molecules coming off surfaces. Zare made the analogy that, while such experiments have become better defined in recent years, our level of understanding of the dynamics is akin to that in reactive scattering perhaps 20 years ago. This reflects the increased theoretical complexity of the problem, as well as the experimental fact that it is necessary to carefully characterize the surface in order to make a meaningful measurement. Zare emphasized studies involving NO, as did J. Barker (IBM). NO-surface interactions have been studied by several groups because NO can be detected conveniently by spectroscopic means. Perhaps the most well studied system is NO-Ag(111). The Ag(111) surface is favorable for detailed study because is is chemically inert and flat. The internal state distribution of NO scattered from this surface has been measured by two groups(Zare and Auerbach and their coworkers) with incident NO beams of different kinetic energies. At high energy, a rotational rainbow and alignment are observed in the scattered molecules. There have been several theoretical explanations of these results, indicating that further

experiments are needed to distinguish among these models. Barker discussed recent results of Rettner, Fabre, Kimman, and Auerbach showing that vibrational excitation in NO/Ag(111) collisions increases with incident energy and surface temperature with an activation energy of (1/4)eV.

D. S. King (NBS) and coworkers have investigated the energy distribution of thermally desorbed NO molecules from Pt(111). The rotational temperature T_{rot} of molecules desorbed from several different sites on this surface is nearly equal to the surface temperature T_s. This behavior is consistent with the known large accommodation coefficient for this system. By contrast, T_{rot} is approximately 1/2 of T_s for NO-Ru, reflecting the role of the desorption dynamics.

G. Comsa (Jülich) described the use of helium beam diffraction as a sensitive probe of surface disorder. This technique relies on the fact that the diminution of the diffraction signal can be related to a scattering cross section for the adsorbate. Moreover, the large size of this cross section implies that the experiment is sensitive to the packing of adsorbates and/or vacancies on the surface. This very sensitive method has been employed to study both repulsive and attractive adsorbate interactions, as well as to map out a 2-dimensional phase diagram of an adsorbate.

A. E. DePristo (Iowa State University) gave an overview of theoretical work on collisions at surfaces. Particularly noteworthy are recent treatments of dissociative adsorption, $T \rightarrow R$ and $T \rightarrow$ phonon energy transfer, nonadiabatic electron transfer, and laser desorption. B. Lundqvist (Chalmers University of Technology) stressed an approach to adsorbate-metal interactions based on the concept that, as a molecule approaches the surface, its antibonding orbital is lowered, splits, and is filled by electron transfer.

E. J. Heller (University of Washington) discussed photodissociation experiments from the point of view of what information is revealed on each of several time scales. The available probes were ordered by increasing time scale as electronic absorption; Raman scattering to fundamentals, low

overtones, and higher overtones; time-of-flight and product-state distributions; and long-time secondary emission.

W. H. Breckenridge (University of Utah) and B. Soep (Université de Paris-Sud, Orsay) discussed reactions of electronically excited metal atoms. Soep presented pioneering experiments on reactions within van der Waals complexes involving Hg atoms. Complexes in the ground electronic state with various species, e.g. H_2, Cl_2, were prepared in a free jet expansion. The Franck-Condon portion of the excited electronic surfaces, on which reaction is energetically allowed, was accessed by optical excitation. In the case of $Hg^{*}\cdot H_2$ differences in reactivity were observed depending on whether the Σ or Π excited state was prepared. Breckenridge compared and contrasted the reactions of the excited $^3P_1$ state of the group 10 atoms with the isotopes of H_2, concentrating in particular on differences in the product metal hydride rotational distribution.

D. R. Yarkony (Johns Hopkins University) presented new efficient methods for calculating the coupling strengths of spin-forbidden and Born-Oppenheimer nonadiabatic processes. In both cases the state-averaged multiconfiguration self-consistent-field method plays an essential role.

The plenary discussions following the lectures were exceptionally vital and provided a strong indication of the current excitement in this field.

The 1985 Conference on the Dynamics of Molecular Collisions was sponsored by the Air Force Office of Scientific Research, the Argonne Universities Association Trust Fund, Cooper LaserSonics, Inc., the National Science Foundation, the Donors of the Petroleum Research Fund (administered by the American Chemical Society), and the Research Corporation.

The successor to this meeting, the 1987 Conference on the Dynamics of Molecular Collisions, will be held in Oglebay Park in Wheeling, West Virginia, on July 12-17, 1987. The conference organizers are Paul J. Dagdigian,

chairman, and William H. Miller (University of California, Berkeley), vice-chairman. Further information can be obtained by writing to Professor P. J. Dagdigian, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218.

1985 Conference on the Dynamics of Molecular Collisions

ADDITIONAL POSTERS

61B S. J. Ulvick, T. C. Maguire, R. F. Curl, P. R. Brooks, and J. H. Spence, Rice Quantum Institute, "Reaction Complex Spectroscopy".

CANCELLED POSTERS

15B, 15C, 18C, 40B, 56C, 58C

ADDITIONAL POSTER INDEX ENTRIES

Armentrout, P. B.	56B	Leone, S. R.	59C
Binkley, J. S.	60A	Maguire, T. C.	61B
Brooks, P. R.	61B	Redmon, M. J.	60A
Butler, L. J.	59A	Spence, J. H.	61B
Chapman, S.	59B	Stewart, B.	60B
Curl, R. F.	61B	Ulvick, S. J.	61B
Donaldson, J.	59C		

ADDITIONAL REGISTRANTS

Dr. Jeremy Frey, University of Southampton, U.K.
Mr. Sid Ulvick, Rice Quantum Institute, Houston
Dr. Donald L. Thompson, Oklahoma State University, Stillwater

CANCELLED REGISTRATIONS

R. Brudzynski, G. Doyen, J. Fenn, D. Thirumalai, G. Tyndall.

Note: The posters for which Thirumalai and Tyndall are the underlined authors will be presented by B. C. Garrett and C. L. Cobb, respectively.

BUSINESS MEETING

There will be a brief business meeting in the Cottonwood Center at 1:15 p.m. Tuesday. Attendance is optional of course. Subjects: 1987 and 1989 meetings.

RETURN BUSES AND VANS (TO SALT LAKE CITY AIRPORT)

There will be a representative of Lewis Brothers Van Service at the registration desk from 1:00 to 3:30 p.m. Wednesday. If you wish to sign up for the main departure bus (12:20 p.m. Friday) or one of the secondary departure times (noon, 1 p.m., 2 p.m., or whenever four or more wish to depart), please do so at the registration desk at this time or earlier in the week. Note: van service is available for groups smaller than 4 at a rate of $40.00/van. For groups of 4 or more the rate is $10.00 per person. Payment is made to the driver.

ASSISTANCE. The following persons are ready to assist you:

* poster session - Paul Dagdigian (vice chairman), Susan Tucker
* registration - Ken Haug
* financial (speakers, scholarship recipients) - David Cochrane
* plenary sessions, other matters, problems - Don Truhlar (chairman)

Ken Haug and David Cochrane will be at the registration desk 1:15-2:00 p.m., Monday-thru-Thursday.

1985 Conference on the Dynamics of Molecular Collisions

Additional post-deadline poster papers

61A ..... A. J. Sedlacek and C. A. Wight, University of Utah, "Infrared Fluorescence Studies of Near Resonant E-V Transfer"

61C ..... F. Crim, University of Wisconsin, "Energy Transfer via Vibrational Predissociation: Relaxation of HF by HF Dimer"

62A ..... D. King, National Bureau of Standards "Vibrational Predissociation of $(NO)_2$"

62B ..... F. Strobel, J. Wronka, R. B. Freas, III, W. Reents, Jr., and D. Ridge, University of Delaware, "Reactions of Metastable Chromium Ion"

62C ..... D. Brenner and B. Garrison, Pennsylvania State University, "A Classical Dynamics Study of the Ion Bombardment of Ice"

1985 Conference on the Dymamics of Molecular Collisions

Final amendments to attendance list

CANCELLATIONS

Y. Lee, B. Srivastava

ADDITIONAL REGISTRANTS

Ms. Cindy Beggs
Department of Chemistry
University of California
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Dr. Christophe Jouvet
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Université Paris-Sud 91405, Orsay Cedex, France

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Department of Chemistry
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CHANGE OF ADDRESS

Dr. Satoru S. Kano
Institute for Laser Science
University of Electro-Communications
Chofugaoka, Chofushi, Tokyo 182, Japan

(2)

1985 Conference on the Dynamics of Molecular Collisions

July 14-19, 1985
Snowbird, Utan U.S.A.

Chairman: Donald G. Truhlar
Vice chairman: Paul J. Dagdigian
Treasurers: Donald G. Truhlar and W. Ronald Gentry

Sponsors: Air Force Office of Scientific Research
Argonne Universities Association Trust Fund
Cooper LaserSonics Inc.
National Science Foundation
Petroleum Research Fund
Research Corporation

Cover Illustration: Two quasiclassical trajectories for $H + H_2 \rightarrow H_2 + H$ as functions of mass-scaled coordinates. The underlying dashed contours are the potential energy surface. The two trajectories begin in the lower right with the same vibrational energy but different phases, they experience a long-lived collision and exhibit features corresponding to the classical analog of a Feshbach internal-excitation resonance, and finally they evolve upwards to the product region with slightly different final vibrational energies. Reference for trajectory calculations: J. W. Duff and D. G. Truhlar, Chem. Phys. 4 (1974) 1.

Final Schedule
Conference on the Dynamics of Molecular Collisions
Snowbird, Utah, July 14-19, 1985
Donald G. Truhlar, Chairman; Paul J. Dagdigian, Vice Chairman

Sunday

5:30 - 7:30 p.m.	Reception. Cottonwood.
5:30 - 7:30 p.m.	Registration. Foyer adjacent to Cottonwood.

Monday

7:15 - 8:15 a.m.	Breakfast. Pavilion.
8:30 - 11:50 a.m.	Session on Reactive Collisions Experimental. Chairman/Discussion Leader: Tom Baer. Cottonwood.
	8:30 Jim Valentini "Overview"
	9:20 Discussion
	9:40 Break
	10:00 Jack Beachamp "Dynamics of Gas-Phase Organometallic Reactions"
	10:40 Discussion
	10:55 Jim Sloan "Energy Partitioning in Gas-Phase Reactions Measured via Low-Pressure Emission Spectroscopy"
	11:35 Discussion
12:15 - 1:15 p.m.	Lunch. Pavilion.
6:00 - 7:00 p.m.	Dinner. Pavilion.
7:30 - 9:55 p.m.	Session on Reactive Collisions Theoretical. Chairman/Discussion Leader: Lionel Raff. Cottonwood.
	7:30 Bill Miller "Overview"
	8:10 Discussion
	8:25 George Schatz "Theoretical Studies of State-to-State Chemistry: A + BC and Beyond"
	9:00 Discussion
	9:10 John Murrell "The General Strategy of the Many-Body Expansion for Potential Functions"

Tuesday

7:15 - 8:15 a.m.	Breakfast. Pavilion.
8:30 - 11:50 a.m.	Session on Vibrational-Rotational Energy Transfer Experimental. Chairman/Discussion Leader: Roger Miller. Cottonwood.
	8:30 Bob Gordon "Overview"
	9:20 Discussion
	9:40 Break
	10:00 Peter Andresen "Inelastic Scattering of $^2\Pi$ Molecules"
	10:40 Discussion
	10:55 Eldon Ferguson "Relaxation and Reaction Rates of Vibrationally Excited Ions in a Selected Ion Flow Drift Tube (SIFDT) and a Wind Tunnel (CRESU)"
	11:35 Discussion
12:15 - 1:15 p.m.	Lunch. Pavilion.
6:00 - 7:00 p.m.	Dinner. Pavilion.
7:30 - 9:55 p.m.	Session on Vibrational-Rotational Energy Transfer Theoretical. Chairman/Discussion Leader: Jim Cross. Cottonwood.
	7:30 David Clary "Overview"
	8:10 Discussion
	8:25 Millard Alexander "Energy Transfer in Collisions Involving Open-Shell Molecules"
	9:00 Discussion
	9:10 Gert Due Billing "Rotational-Vibrational Energy Transfer in Small Molecules"

Wednesday

7:15 - 8:15 a.m.	Breakfast. Pavilion.
8:30 - 11:50 a.m.	Session on Collisions at Surfaces Experimental. Chairman/Discussion Leader: Mark Cardillo. Cottonwood.
	8:30 Dick Zare "Overview"
	9:20 Discussion
	9:40 Break
	10:00 George Comsa "Adsorbates and Surface Defects Seen by Thermal He Scattering"
	10:40 Discussion
	10:55 David King "Energy Distributions in Thermally Desorbed Molecules"
	11:35 Discussion
12:15 - 1:15 p.m.	Lunch. Pavilion.
6:00 - 7:00 p.m.	Dinner. Pavilion.
7:30 - 9:55 p.m.	Session on Collisions at Surfaces Theoretical. Chairman/Discussion Leader: Barbara Garrison. Cottonwood.
	7:30 Andrew dePristo "Overview"
	8:10 Discussion
	8:25 John A. Barker "Gas-Surface Dynamics: Classical and Quantal Theories of Inelastic Effects"
	9:00 Discussion
	9:10 Bengt Lundqvist "Electronic Factors for Conservative and Dissipative Forces in Molecule-Surface Dynamics"

Thursday

7:15 - 8:15 a.m.	Breakfast. Pavilion.
8:30 - 12:10 a.m.	Minisymposium on Collisional and Collision-Free Intermode Energy Transfer. Chairman/Discussion Leader: Bill Reinhardt. Cottonwood.
	8:30 Eric Heller "Intramolecular Dynamics - What do Correlation Functions and their Associated Spectroscopies Tell Us?"
	9:05 Discussion
	9:20 Doug McDonald "Intramolecular Energy Transfer: Where Does the Energy Go?"
	9:55 Discussion
	10:10 Break
	10:30 Alan Knight "Vibrational Relaxation Induced by Very Low Energy Collisions: The Case for Enhancement of the Cross Section"
	11:05 Discussion
	11:20 Charlie Parmenter "Some Connections Between Collisional and Collision-Free Vibrational Flow in Large Polyatomics"
	11:55 Discussion
8:00 - 11:00 p.m.	Poster session. Chairman: Paul Dagdigian. Alpine/Plaza.

Friday

7:15 - 8:15 a.m.	Breakfast. Pavilion.
8:45 - 11:15 a.m.	Session on Processes Involving Electronic Excitation. Chairman/Discussion Leader: Jim Muckerman. Cottonwood.
	8:45 Bill Breckenridge "Rotational State Distributions of Products of Reactions of Electronically Excited Atoms"
	9:20 Discussion
	9:35 B. Soep "Chemical Reactions of van der Waals Complexes"
	10:10 Discussion
	10:25 David Yarkony "Electronic Structure Aspects of Nonadiabatic Processes in Molecular Systems"
	11:00 Discussion
11:15 - 12:15 a.m.	Lunch.
12:20 p.m.	Bus departs for airport.

ABSTRACTS OF PLENARY LECTURES

Note: There are no abstracts for the overview lectures.

Energy Transfer in Collisions Involving Open-Shell Molecules*

Millard Alexander
Department of Chemistry
University of Maryland
College Park, Maryland 20742

Collisions involving molecules with unpaired electrons present a wealth of features not accessible in closed shell systems, since the orbital motion of the collision partners can couple not only with the rotation of the nuclei of the target molecule, but also with the electronic orbital and/or spin of the unpaired electrons. In recent years there has been considerable interest, both theoretical and experimental, in these systems. One of the most exciting aspects of this field has been the discovery of general collisional propensity rules, according to which certain transitions between the various multiplet components of the molecular rotational levels will be strongly favored. These propensity rules, which were derived by a formal analysis of the quantum scattering equations, have now been confirmed by a number of close-coupled calculations as well as by several recent experimental studies, involving both molecular beam as well as laser double resonance techniques.

We shall present an overview of areas of current theoretical and experimental interest in this field, concentrating on the following specific topics:

1. Collisional energy transfer between molecular electronic states. Almost all previous work in collision induced energy transfer has involved the study of processes in which the molecular electronic state has remained unchanged. Over the years there has been some experimental interest in E-E energy transfer, which has been interpreted with simplistic models. As we will discuss, it is now possible to treat completely rigorously the general case of electronically inelastic collisions, and to derive propensity rules for this type of process. This work will be reviewed and related to recent double resonance experiments on N_2^+ and CN.

2. Symmetry and spin-orbit effects in collisions of NO with surfaces. Several experiments have revealed anomalous and subtle effects in the final state Λ-double and spin-orbit level populations in collisions of NO with Ag(111) surfaces. These experiments will be interpreted in terms of interference effects in the collision process, involving, in a semiclassical picture, trajectories which sample the two electrostatic surfaces which result from the interaction of a $^2\Pi$ molecule with a surface. Recent scattering calculations based on a realistic description of these surfaces will be described. In principle the scattering of open-shell molecules from surfaces can be used to probe the intimate details of the binding of important radicals to surfaces.

* Research supported by the National Science Foundation, Grant CHE84-08528 and by the U. S. Army Research Office, Grants DAAG29-84-G-0078 and DAAK29-85-K-0018.

Inelastic scattering of $^2\Pi$ molecules

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The basic principles of rotational energy transfer in collisions of molecules without electronic structure seem to be rather well understood. This may be due to the fact that the only inelasticity that can occur is rotational excitation. For molecules with electronic structure the situation is more involved, because other (electronic) transitions are possible, which modify the picture of rotational energy transfer considerably.

Here, we consider the collisions of the $^2\Pi$ molecules OH and NO with various partners. For example, in the collisions of OH with H_2, the multiplet conserving transitions have to be distinguished from the multiplet changing collisions:

$$OH\,(^2\Pi_{3/2}, N=0) + H_2 \longrightarrow OH(^2\Pi_{3/2}, N', \Lambda') + H_2 \quad \text{multiplet conserving}$$
$$\searrow OH(^2\Pi_{1/2}, N', \Lambda') + H_2 \quad \text{multiplet changing}$$

In both cases rotational excitation and Λ-doublet transitions occur. Propensity rules play an important role and lead to selective population of Λ-doublet states in the case of OH. Among the Λ-doublet states in $^2\Pi_{1/2}$ an inversion is found, which yields a pump mechanism for stellar astronomical OH masers.

The collisions are studied in a cross beam scattering setup with pulsed nozzle beams. In both cases the molecules are cooled by rotational relaxation in a nozzle beam to the lowest quantum state. This implies, that not only the rotational groundstate is obtained, but also that only one multiplet state is prepared in the experiment. In the scattering center, OH or NO is excited by collisions to higher lying states. The population in these states is analyzed by Laser Induced Fluorescence.

The nascent state distributions for rotational-, multiplet and Λ-doublet states are measured and interpreted both qualitatively and quantitatively.

GAS-SURFACE DYNAMICS; CLASSICAL AND QUANTAL THEORIES OF INELASTIC EFFECTS, J. A. Barker, IBM Research Laboratory, San Jose, California 95193.

ABSTRACT: The dynamics of energy exchange between gas atoms and crystal surfaces, with consequent trapping and desorption, is discussed in terms of a simple classical model for the gas-surface potential involving motion in a conservative attractive potential and fast energy-exchanging collisions between gas and surface atoms. Equations for the velocity distributions of atoms leaving the surface after N hops are derived and used to study the approach to the asymptotic steady state for N large. Residence time distributions are calculated, and for high incident beam energies these show a pronounced peak at small residence times (direct inelastic scattering) together with a decay at large residence times which is ultimately exponential. Velocity distributions for trapping/desorption and direct inelastic scattering are calculated and compared with experimental time-of flight distributions. The implications of these results for the kinetics of physisorption and chemisorption are discussed. In addition to these classical results for heavy-atom scattering, some quantum-mechanical results on Debye-Waller factors in helium scattering, calculated using the formulation of Levy and Suhl together with numerically calculated trajectories and surface correlation functions, will be presented.

Dynamics of Gas-Phase Organometallic Reactions

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Gas-phase studies of the reactions of small molecules at transition metal centers have provided a rich harvest of highly speculative reaction mechanisms. Traditional mechanistic probes, such as isotopic labeling, have served mainly to indicate the complexity of "simple" processes. For example, dehydrogenation of alkanes occurs not only by removal of H_2 from adjacent carbons, but by 1,3- and 1,4-elimination processes as well. We have explored the use of product translational energy distributions to provide additional insights into these and other organometallic reaction mechanisms. The final step in a complex mechanism is often postulated to involve reductive elimination of a small molecule from a transition metal center. Product translational energy distributions have been used to characterize the potential energy surface in this region for processes involving H-H and C-H bond formation. The initial interaction of a transition metal ion with a small molecule may lead to several distinct reaction intermediates which decay at different rates. An examination of the decay kinetics provides insights into the number of such intermediates and the specific products into which they decay. A variety of techniques have been developed to prepare stable reaction intermediates which can be examined using spectroscopic probes. For example, in contrast to studies of bimolecular processes in which chemically activated intermediates can decompose to yield several reaction products, IR multiphoton activation of stable intermediates allows the lowest energy pathway to be identified. Several examples of these studies will be presented, along with an overview of current endeavors in this field.

VIBRATIONAL-ROTATIONAL ENERGY TRANSFER IN SMALL MOLECULES

Gert Due Billing

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This lecture will discuss recent work on vibrational/rotational energy transfer in small molecules.

ROTATIONAL STATE DISTRIBUTIONS OF PRODUCTS OF REACTIONS OF ELECTRONICALLY EXCITED ATOMS.

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Excited atoms may dissipate their electronic energy collisionally in a variety of ways. Of particular interest to chemical physicists are the cases in which electronic excitation facilitates chemical reaction. In this talk, the disposal of electronic energy into the rotational quantum states of diatomic chemical products will be discussed. In particular, the reactions of various excited atomic states with the molecules H_2, HD and D_2 will be compared and contrasted.

"Thermal He scattering from disordered surfaces: a new analytical tool"

George Comsa

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The surface scattering of thermal He beams exhibits two particular, apparently contradictory features: an unusually high sensitivity for the presence of adsorbates and/or defects, and a completely non-damaging character of the interaction. The combination of these features was susceptible to provide a valuable, surface sensitive analytical tool. However, it was not until the sensitivity was rationalized by introducing a cross section for diffuse scattering ($\Sigma \approx 10^2$ Å^2 per admolecule) and the origin of the large size of Σ was uncovered that the capabilities of the new tool could be exploited. In the last couple of years these remarkable capabilities were demonstrated in surface investigations ranging from adsorbate kinetics at coverages down to 0.1%, over 2D-Phase transitions, to dynamics of the sputtering-annealing process including the measurement of sputtering yields.

The lecture will present first the basic features of He scattering from close packed surfaces and of the influence of adsorbates and vacancies on the specular beam intensity. Then, the philosophy of the use of He beams for the investigation of disordered surfaces will be outlined. Finally, the application of the method to the study of the adsorption-desorption kinetics and of the surface diffusion of adsorbates will be discussed in detail and exemplified for the systems H and CO on Pt(111).

Relaxation and Reaction Rates of Vibrationally Excited Ions in a Selected Ion Flow Drift Tube (SIFDT) and a Wind Tunnel (CRESU)

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The application of the SIFDT and CRESU systems for ion-molecule studies and their application to several problems relevant to collision dynamics and reaction mechanisms will be discussed. Measurements of vibrationally excited ions with neutrals can be obtained in the SIFDT. The charge-transfer of several triatomic ions with diatomic neutrals is found to be substantially enhanced by vibrational excitation in the ion bending modes. Rotational excitation of the ions has no significant effect on rate constant. Some exothermic proton and H-atom transfer reactions are found to be inhibited by ion vibrational excitation. Several O^- transfer reaction rate constants, e.g. for $CO_3^- + SO_2 \rightarrow SO_3^- + CO_2$, are found to depend neither on vibrational nor rotational state of the ion. Ion vibrational excitation and deexcitation rate constants in neutral collisions can be determined. A recent application of the SIFDT has allowed systematic measurements of vibrational relaxation of $O_2^+(v=1)$, $O_2^+(v=2)$, $N_2^+(v)$ and $NO^+(v)$ ions from thermal energy to ~ 1 eV relative kinetic energy with a number of neutral quenchers. These measurements yield intramolecular energy transfer rates in transient ion-molecule complexes, analogous to vibrational predissociation in van der Waals molecules (if one accepts our model). The SIFDT also allows a comparison of the dependence of rate constants on relative reactant kinetic energy as well as temperature. This comparison gives an insight into the reaction dynamics and the extent of energy pooling. The CRESU technique allows the measurement of both binary and three-body association reactions down to temperatures as low as 8K. The three-body rate constants allow a determination of intermediate complex lifetimes. The potential of these techniques will be illustrated by the ion-molecule reaction $O_2^+ + CH_4 \rightarrow H_2COOH^+ + H$, where both the SIFDT and CRESU techniques have been brought to bear on one reaction to provide a very detailed picture of the complicated reaction mechanism. The rate constant has been measured as a function of O_2^+ vibrational states v = 0,1,2,3, as a function of temperature from 20K to 560K, as a function of kinetic energy at several gas temperatures (up to ~1eV at 300K), and for all the deuterated isotopes of CH_4. The reaction involves the sequential (a) formation of a very long-lived orbiting complex, (b) hydride ion transfer to O_2^+, and (c) H-atom ejection, occurring on a double minimum potential surface. Steps (b) and (c) have off-setting isotope effects, leading to a near statistical isotopic distribution of products. Step (b) is rate controlling, leading to a near linear increase in rate constant with H for CH_nD_{4-n}.

INTRAMOLECULAR DYNAMICS - WHAT DO CORRELATION FUNCTIONS AND THEIR ASSOCIATED SPECTROSCOPIES TELL US?

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Abstract

New perspectives on correlation functions for collisional (e.g. time-of-flight) and radiative (e.g. infrared emission) spectroscopies tell us much more about the dynamical information content in spectroscopic measurements of both isolated and condensed phase molecules. Classical trajectory methods can sometimes be applied successfully to understand and predict spectra, but sometimes they fail miserably. Semiclassical methods help but still leave large gaps in what we can do accurately. Semiclassical - *ab initio* mixed methods help considerably but problems involving many degrees of freedom and long time dynamics remain out of reach.

Now results on infrared radiation cascades and rotational spectra will be described. The spectroscopic signatures of resonances and complete IVR will also be discussed.

ENERGY DISTRIBUTIONS IN THERMALLY DESORBED MOLECULES*

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Thermal desorption is one method for investigating the molecule-surface interaction. Statistical mechanical models would predict molecules desorbing from surfaces to be characterized by equilibration with the surface. Expectations based on molecular dynamics would allow for variation between different degrees of freedom (e.g., rotation, vibration or translation) and not require any fixed relation to the initial surface temperature. Results will be presented on the internal states distribution of NOthermally desorbed from Pt(111). In addition, new results on co-adsorbed systems of NO and CO on Pt will be presented and discussed.

The thermal desorption spectrum of NO/Pt(111) is dominated by three major features, occuring at surface temperatures of 200, 340 and 385 K. The peak temperatures for a fixed NO coverage are dramatically shifted by co-adsorption of CO due to adsorption site competition. For the co-adsorbed system, the resulting thermal desorption depend on the ordering of adsorption. Under all conditions the NO rotational temperature is nearly equal to the surface temperature. In experiments where CO is post-adsorbed on a partial coverage of NO, the rotational temperature appears to be about 5% lower than for neat NO desorption at the same surface temperature.

Doppler studies are currently underway for these systems. These experiments will give both the kinetic energy of the desorbing NO and also the angular flux distributions as a function of internal state. The results of these experiments will hopefully add insight into the relative importance of statistical mechanics vs molecular dynamics in controlling heterogeneous processes such as thermal desorption.

* Work supported, in part, by Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division.
# NRC/NBS postdoctoral fellow.

Paper to be presented at the 1985 Conference on the Dynamics of Molecular Collisions, Snowbird, Utah.

VIBRATIONAL RELAXATION INDUCED BY VERY LOW ENERGY COLLISIONS: THE CASE FOR ENHANCEMENT OF THE CROSS SECTION

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State-to-state vibrational energy flow from selected vibrational levels in S_1 benzene and naphthalene has been explored using a seeded supersonic expansion of argon to provide very low collision energies in the range 1 - 20 cm^{-1}. Collisions between the polyatomic and the monatomic carrier gas lead to depopulation of the initially excited vibrational state. Time-resolved dispersed fluorescence spectra provide the means by which population transfer to other vibrational levels in the polyatomic manifold may be monitored. Absolute rates for state-to-state vibrational relaxation are obtained from measurements of the intensities of growth bands that appear in the dispersed fluorescence spectrum. By setting the crossing point of the excitation laser at a variety of distances downstream from the nozzle exit, data are obtained for various mean translational temperatures. Consideration has been given to the influence of velocity slip between seed and carrier gas. Experimental tests as well as computational modelling of our expansion verify that the influence of velocity slip is negligible in our measurements with argon as carrier gas. The absolute rates for vibrational deactivation of the $8(b_{1g})^1$ level in naphthalene and the 6^1 level in benzene, measured as a function of average collision energy, are compared with binary collision rates for Lennard-Jones spheres whose interaction is governed by an effective potential that includes the centrifugal barrier. For both benzene-Ar and naphthalene-Ar, the ratio between the experimental rate and the Lennard-Jones rate increases by a factor of $\sim$4 as the mean relative collision energy drops from $\sim$20 cm^{-1} to $\sim$2 cm^{-1}. The implications of these findings will be debated.

1985 Conference on the Dynamics of Molecular Collisions
Snowbird, Utah, July 14-19, 1985

ELECTRONIC FACTORS FOR CONSERVATIVE AND DISSIPATIVE FORCES IN MOLECULE-SURFACE DYNAMICS

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Description of the dynamics of atoms and molecules at surfaces, either by quantum-mechanical scattering theory or by the equations of irreversible thermodynamics, requires a physically sound input of conservative and dissipative forces to give meaningful results. Compared with gas-phase dynamics, there are several features distinguishing surfaces, both static, such as the geometry of the surface and the extended nature of the substrate electron states, and dynamic ones, such as the low-lying excitation spectra of phonons and electron-hole pairs. This paper is meant to be a brief attempt to show that a coherent picture of electronic aspects of adsorption and surface reactions is developing.

The origin is an increasing understanding of the adsorbate-induced electron structure and potential-energy surfaces of adsorbates. For chemisorption, such results have been derived from, e.g., self-consistent Kohn-Sham calculations on atoms and molecules adsorbed on model surfaces. For instance, the weakening and breaking of molecular bonds on metal surfaces get their explanation in terms of the lowering (raising), broadening and filling of molecular affinity (ionization) levels, occuring for molecules close to the surface. The conceptual picture has recently been extended to transition metals by the effective-medium and similar schemes. Potential-energy surfaces can there be simply calculated with a practical accuracy, and the role of the d-electrons can be understood. Trends in chemisorption properties and reaction rates along the transition-metal series can be explained. Variations between different faces of the same substrate, and the roles of defects, like steps, promoters and poisons can be described.

As one of several possible mechanisms for the damping of the motion of chemisorbed species on metal surfaces, the energy transfer into electron-hole-pair excitations of the substrate has to be considered. First-principles model calculations indicate that the corresponding damping rates of vibrational modes of light adsorbates may be of the same order of magnitude as measured vibrational linewidths, in particular for reactive adsorbates that induce electronic states at the Fermi level of the metal. For light atoms impinging on metal surfaces the electronic mechanism seems to be able to accommodate typical thermal energies.

INTRAMOLECULAR VIBRATIONAL RELAXATION: WHERE DOES THE ENERGY GO?

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We have observed infrared pure vibrational fluorescence spectra from molecules excited with an infrared Optical Parametric to single vibrational, and in some cases, rovibrational levels. Analysis of the resulting fluorescence spectra allows determination of the final fate of the deposited energy. Typical molecules studies are methyl formate, dimethyl ether, 1,4-dioxane and 2,3-dihydrofuran.

THE GENERAL STRATEGY OF THE MANY-BODY EXPANSION FOR POTENTIAL FUNCTIONS

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The many-body expansion of the potential function of an N-atom polyatomic molecule takes all R-body terms ($R < N$) from the potentials (assumed known) of the R-atom dissociation limits so that only the N-body terms have to be determined for each new system. The method has been shown to provide a useful strategy for tri- and tetra-atomic systems when a global representation of the whole surface is required. Multi-valued functions are required to represent surfaces which have more than one dissociation channel for a particular fragmentation and these are represented by the eigenvalues of matrices. The elements of these matrices can be uniquely defined by the condition that only N-body terms occur in the off-diagonal elements.

The general strategy, together with many applications is described in a recent publication, "Molecular Potential Energy Functions", by Murrell, Carter, Farantos, Huxley and Varandas, J. Wiley, 1984.

Abstract for 19th Conference on Dynamics of Molecular Collisions

SOME CONNECTIONS BETWEEN COLLISIONAL AND COLLISION-FREE VIBRATIONAL FLOW IN LARGE POLYATOMICS.

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An emerging set of data concerning state-selected vibrational energy flow within S_1 p-difluorobenzene (pDFB) is beginning to show some connections and contrasts between collisional and collision-free processes. State-to-state 300K bulb experiments by David Nesbitt using Ar collisions reveal the strong propensities typical of polyatomic transfers. They are modelled well by benzene-type propensity rules with one modification. The matrix element for activity in the low frequency fluorine bend ν_{30}' must be increased relative to the uniform values used for all other modes. Thus ν_{30}' is an accelerating mode for collisional energy transfer. Karl Freed has completed a quantitative study of the psec collision free IVR dynamics from eleven levels in S_1 pDFB. The IVRs are well modeled with radiationless transition dynamics (inter-molecular anharmonical case). The dynamics have substantial mode selectivity, with IVR time scales ranging from about 20 to 800 psec. Interestingly, levels containing quanta of ν_{30}' display comparatively fast IVR, so it is clear that ν_{30}' is also an accelerating mode for collision-free IVR. Enhanced average coupling matrix elements are associated with this ν_{30}' activity. A third "half-collisional" probe of vibrational energy flow is derived from jet studies of vibrational predissociation from pDFB-Ar van der Waals complexes underway by David Nesbitt and Dmitrii Krajnovich. The observed level-to-level flow patterns observed in these processes are quite different than those realized from the 300K bulb-collision experiments.

Theoretical Studies of State to State Chemistry: A + BC and Beyond

George C. Schatz

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In this talk we discuss several recent advances in theoretical methodology which enable the study of state to state chemistry in gas phase collisions at previously unobtainable levels of sophistication.

For atom-diatom reactions, for example, it is now possible to calculate accurate three dimensional quantum cross sections for systems that are considerably more complex than $H + H_2$. One of the keys to this development is a coupled channel distorted wave (CCDW) method[1] which is capable of calculating exact quantum cross sections at energies near or below threshold where tunnelling dominates. Results for $O + H_2$, D_2, HD, DH and for Cl + HCl will be presented which show the versatility of this method, and also its usefulness for assessing the accuracy of approximate quantum and classical methods. Exact quantum scattering calculations based on matching methods have also been extended beyond $H + H_2$, although their domain of application is more limited than CCDW because of coordinate system restrictions. Nevertheless, much can be learned from such calculations, and in this talk we will emphasize studies of $D + H_2$, $H + D_2$ and $\mu + H_2$.

For systems with four or more atoms, the quasiclassical trajectory method is still the workhorse of chemical dynamics (but maybe not for much longer). Even using trajectories, however, it is still very difficult to do detailed state to state dynamics studies because of the difficulties associated with defining polyatomic molecule semiclassical eigenstates. There has been much progress recently, however, including one method[2] which enables the determination of eigenvalues for rotating Fermi-resonant triatomic molecules. This has enabled us to study the very fundamental $H_2^+ + H_2 \rightarrow H_3^+ + H$ system, the dynamics of which turns out to be both rich and surprising.

1. G.C. Schatz, L.M. Hubbard, P.S. Dardi and W.H. Miller, J. Chem. Phys. 81, 231 (1984).

2. C.W. Eaker and G.C. Schatz, J. Chem. Phys. 81, 2394 (1984); C.W. Eaker, G.C. Schatz, N. DeLeon and E.J. Heller, J. Chem. Phys. 81, 5913 (1984).

ABSTRACT

Energy Partitioning in Gas Phase Reactions Measured via Low-Pressure Emission Spectroscopy.

J.J. Sloan
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Experimental techniques of increasing sophistication are being developed to explore the detailed dynamics of gas phase reactions. As a result, the range of processes accessible to study has gradually expanded from reactions forming hydrogen halides to ion/molecule reactions and the reactions of free radicals and electronically excited atoms. The two experimental techniques which have been responsible for the major advances are laser induced fluorescence and low-pressure infrared emission spectroscopy.

Recently, time-resolved Fourier transform spectroscopy has been incorporated in the latter experiment, providing a capability for aquisition of complete product spectra as a function of time after the excitation event. A brief summary of some technical aspects of this experiement will be given. Energy partitioning in several reactions and energy transfer processes involving $O(^1D_2)$ atoms have been measured using this technique; the results will be discussed in the context of existing dynamical measurements of these processes.

CHEMICAL REACTIONS OF VAN DER WAALS COMPLEXES

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We have developed a new method which allows the direct access to the reaction intermediates and to study their time evolution. The collision is replaced by an half collision where the reactants are frozen in the ground state of a Van der Waals complex and an optical excitation brings the system to the reactive surface.
Then, all the collisionals parameters are defined : internal and translational energies are nearly zero, and the geometry is defined.

Two examples are given :
In the study of $Hg\ (^3P_1) + Cl_2 \longrightarrow HgCl\ (B^2\Sigma^+) + Cl$,
the ionic intermediate of the reaction is spectroscopicaly observed.[1]
For the reaction $Hg\ (^3P_1) + H_2 \longrightarrow HgH + H$, a difference of reactivity between the electronics states of the complex has been observed, which is in a collision experiment a polarisation effect.[2]

References :

1. C. Jouvet and B. Soep, Chem. Phys. Lett. 96, 426 (1983)
2. C. Jouvet and B. Soep, Laser Chem. 5, 157 (1985)

Abstract: Dynamics of Molecular Collisions
14-19, July 1985
Snowbird, Utah

Title: Electronic Structure Aspects of Nonadiabatic Processes in Molecular Systems

Speaker: David R. Yarkony

We will be concerned with two classes of nonadiabatic processes, those which result from nuclear motion and those which result from a breakdown of spin as a good quantum number. In each instance we will outline recent methodological advances made in collaboration with G. F. Adams, B. H. Lengsfield, S. J. Havriliak and P. W. Saxe of the Ballistics Research Laboratory, which have significantly improved our ability to treat these classes of problems. To be discussed is a method in which the nonadiabatic coupling matrix elements $\langle \Psi_J(\underset{\sim}{r};\underset{\sim}{R}) | \frac{\partial}{\partial \underset{\sim}{R}} \Psi_I(\underset{\sim}{r};\underset{\sim}{R}) \rangle_r$ are evaluated directly from state averaged MCSCF/CI wavefunctions using direct gradient methods, i.e. without recourse to finite differences. Spin forbidden processes, in particular radiative decay, will be discussed using a new approach which obviates the need for a complete diagonalization of the zeroth order Hamiltonian, making the procedure amenable to large scale CI wavefunctions.

Applications will include nonadiabaticity due to nuclear motion in reactions of the form:

$$Me + X\text{-}Y \rightarrow MeX + Y$$

where Me is an alkaline earth (or alkali) atom and X is a halogen and Y is a halogen or hydrogen. Spin forbidden radiative processes $(^1\Sigma^+, {}^1\Delta) \rightarrow {}^3\Sigma^-$, in NF and related systems will be discussed.

POSTER SESSIONS

POSTER SESSIONS

The Alpine/Plaza area is reserved for our group from Monday morning to Friday noon. Please put your posters up Monday afternoon and leave them up till at least 11:00 p.m. Thursday.

Clearly posters may be discussed informally at any time. Formal presentations will occur Thursday evening, and poster presenters are asked to be at their stations at the following times:

A posters	8:00- 9:00 p.m.
B posters	9:00-10:00 p.m.
C posters	10:00-11:00 p.m.

1A

RECOMBINATION OF CARBON AND OXYGEN ON A CATALYST SURFACE

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A classical trajectory study has been carried out of the oxidation of carbon adsorbed on the (111) face of a platinum crystal via the Langmuir-Hinshelwood mechanism. The exact motions of the carbon, oxygen and top twenty-four platinum atoms are followed using an empirical interaction potential, with periodic boundary conditions being used to mimic an infinite surface. Angular and energy distributions for the nascent CO molecules escaping from the surface have been calculated and compared with reported experimental results. A particular emphasis is placed on an investigation of the sensitivity of the product distributions to the manner in which carbon and oxygen combine and the role played by platinum in the recombination.

1B

Energy Partitioning in the Reaction of $O(^1D)$ with CO

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Time-resolved Fourier transform infrared spectroscopy has been used to study the energy partitioning in the reaction of $O(^1D)$ atoms with CO. $O(^1D)$ atoms are generated in a low pressure infrared chemiluminescence apparatus by the photolysis of O_3 using a high-repetition rate KrF excimer laser. The infrared spectrum at various time delays after the photolysis pulse is measured using a Fourier transform spectrometer. Instantaneous populations of the CO vibrational levels are obtained by measuring the temporally-and spectrally-resolved $CO(\Delta v = -1)$ spectra. The results, which indicate that there is substantial $CO(v',J')$ excitation, will be compared with existing measurements on this system.

/C

PHOTODISSOCIATION SPECTROSCOPY AND PHOTOFRAGMENTATION DYNAMICS OF MASS SELECTED CLUSTER IONS

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Cluster ions are formed in a free jet expansion around an ionic chromophore with a known absorption spectrum. Following mass selection in a TOF mass spectrometer, the clusters are photodissociated via absorption of a laser photon by the chromophore. Charged photofragmentation products are mass analyzed in a second, "reflectron," TOF and the distributions are investigated as a function of both photon energy and cluster size. The identity of these daughter ions gives structural information about the cluster and insight into the dynamics of the photodissociation event.

Data are presented for photofragmentation of $(CO_2)_n^+$ clusters, n=2-26, at 1064, 650 and 532 nm. The product distributions are narrow and reveal a constant loss of neutral CO_2 monomers above n=20. The number of neutrals lost is found to be proportional to the photon energy. A mechanism for the photodissociation involving sequential loss of monomers is presented.

Fragmentation patterns are also presented for $Br_2^-(CO_2)_n$, n=2-12. This system provides a unique opportunity to study the process of geminate recombination as a function of the number of CO_2 ligands and energy absorbed by the cluster.

RESONANCES IN SYMMETRIC COLLINEAR REACTIONS OF HYDROGEN ISOTOPES

Timothy G. Mattson[+] and Roger W. Anderson
Chemistry Board of Studies
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2A

Efficient procedures for carrying out reactive scattering calculations in hyperspherical coordinates are developed and applied to the symmetric, collinear H + LH (L = Mu,H,D,T) reactions. These reactions cover a range of mass skewing angles and the effects of the skew angle on the dynamics are presented. Resonance positions are compared for the various reactions demonstrating similar underlying dynamics. The DIVAH model, that adds diagonal corrections to the angular adiabatic potentia's, is shown to be very accurate for predicting resonance positions for small skew angle systems. For the heavier, large skew angle systems the DIVAH model is not accurate but is useful for classifying resonances as shape or Feshbach. The calculations are accelearated by limiting the coupling between channels. This is done by forcing the interval to interval adiabatic transformation matrices to be banded. This procedure also leads to information about the degree of channel coupling needed to fully describe the dynamics. Tri-diagonal transformation matrices are shown to give accurate results for the smallest skew angle system and good results for the heavier systems. Penta-diagonal matrices yield accurate results for all the systems.

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SPECTRAL AND TIME RESOLVED CHEMILUMINESCENCE

2B

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Energy disposal in the Ba + N_2O = BaO + N_2 chemiluminescent reaction is measured as a function of the internal energy of the N_2O reactant under single collision conditions. The internal excitation is provided by heating an effusive N_2O source. The spectrum of the BaO emission shows marked increases for the band features at wavelengths shorter than 500 nm. Little change is found for longer wavelengths. Time resolution of the emission is performed by spectrally resolving fluorescence at different distances from the intersection of the Ba and N_2O beams. The spectra of the longer lived emitters is quite different from that of the shorter lived emitters. The strongest feature in the short life spectrum vanishes in the long life spectrum.

Simulations of the spectra are performed with a program that adjusts vibrational populations for various excited states of BaO. The program uses RKR Franck-Condon factors, statistical rotational distributions, Honl-London factors, monochromator resolution convolution, and splines to give unbaised vibrational distributions. Simulations that assume that the emission occurs from the A and A' states of BaO do not reproduce the interesting blue end of the spectra. Simulations of relaxed beam-bulb spectra show that the A state can adequately account for the red emission. Since the single collision, short wavelength band positions are not precisely simulated by the assuming A' state emission, we conclude that another electronic state of BaO must be involved in the chemiluminescence.

2C

Studies of the Chemistry of Vanadium Cluster Ions

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ABSTRACT

Sputtering with rare gas ion projectiles is used to produce singly-charged clusters of vanadium and vanadium oxides ($V_nO_m^+$) in the gas phase. Storage in a buffer gas using radio-frequency ion traps can be used to cool the hot ions produced in the source. The beam of clusters is then allowed to react with a variety of small molecules and cross sections for ionic product formation are measured.

3A

MOLECULAR BEAM STUDIES OF ANISOTROPIC INTERACTIONS AND THEIR THEORETICAL ANALYSIS

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Integral and differential cross sections measured in this laboratory for interactions between various atoms and simple molecules provide information on anisotropic intermolecular potential.

The analysis of data is based on a quantum mechanical treatment of alternative coupling schemes and decoupling approximations which are also of interest for the use of this information for the description of inelastic and reactive collisions.

Key refernces are, for atom-atom integral cross sections: V. Aquilanti et al., in "Electronic and Atomic Collisions", Invited Papers, J. Eichler et al., Eds., Elsevier (1984); for atom-molecule diffrential cross sections: P. Casavecchia et al., Chem. Phys. Letters 112, 445 (1984); for an outline of a discrete angular representation: V. Aquilanti and G. Grossi, Lettere al Nuovo Cim., 42, 157 (1985).

3B

Ion Beam Studies of V^+ and VO^+ Chemistry

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The reactions

(1) $V^+ + ROH \rightarrow$ products

(2) $VO^+ + RH \rightarrow$ products

where R = CH_3 and H, have been studied in a guided ion beam apparatus. These systems are examples of processes where one can probe a transient reaction intermediate, here $[VROH^*]^+$, from more than one initial reactant state.

We have measured the translational energy dependence of the cross sections for reactions 1 and 2. We find that when R = H, the oxidation of D_2 by VO^+ to make $V^+ + D_2O$ and the reverse reaction of reduction of water by V^+ both occur. When R = CH_3, however, while VO^+ is observed to oxidize methane to methanol, the reverse reaction is not seen.

By interpreting the thresholds for endothermic processes, heats of formation of several transition metal ion complexes are obtained. The effect of the oxide ligand on transition metal carbon and metal hydrogen bond strengths is of particular interest.

3C

Molecular Photodissociation

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A scattering formalism using both adiabatic and diabatic representations is utilized to give a multi-channel description of angular distributions in molecular photodissociation. Branching ratios are given as a function of J, where J is the quantum number for the total angular momentum. Cross-sections are presented and compared. Results are given for the alkali-halides, which exhibit a mixture of ionic and covalent character.

COLLISIONAL EFFECTS ON THE REVERSE SATURABLE ABSORPTION OF SHORT LIGHT PULSES

4A

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The use of molecules which possess an excited state absorption cross section, $\sigma^*(\lambda)$, larger than the ground state absorption cross section, $\sigma(\lambda)$, at a particular incident wavelength of light, λ, (and a number of other properties) as pulse energy limiters, pulse shortners, power limiters, and pulse smoothers has recently been described.[1,2] Such molecules have been called reverse saturable absorbers in contradistinction to saturable absorbers, whose absorption decreases with increased population of the excited state.

We describe the absorption characteristics of polarized light pulses of short temporal duration in reverse saturable absorbers. The effects of rotational diffusion, pulse depletion, finite pulse propagation time, and transition dipole moment orientation are properly treated. Significant enhancement of the reverse saturation due to excited state absorption results when the ground and excited state absorption dipole moments are parallel. We focus on the collisionally induced rotational diffusion of the molecules, and its effect on the pulse absorption and the subsequent fluorescence.

To carry out this study, we develop and solve the set of coupled partial differential equations describing the electric field propagation and the rate equations for the effective concentrations of molecules with transition dipole moments parallel and perpendicular to the electric vector of the field. Our treatment explicitly treats the effects of strong pulse absorption and finite temporal pulse widths, since these effects are crucial for many reverse saturable absorption applications.

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4B

TIME-RESOLVED OPTOACOUSTIC MEASUREMENTS OF THE VIBRATIONAL RELAXATION OF HIGHLY EXCITED MOLECULES. Kenneth M. Beck, Andrzej Ringwelski, and Robert J. Gordon, Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60680.

Two real-time optoacoustic techniques were used to study the VT relaxation of highly excited polyatomic molecules. In the first method a microphone placed at the wall of a long cylinder measured the interference pattern of the acoustic waves which were generated as the excited gas relaxed. In the second method a high frequency piezoelectric ceramic, placed near the center of a large chamber, measured the compression and rarefaction components of a single acoustic wave. Both techniques were used to determine how the rate of vibrational relaxation depends on the amount of energy initially contained in the molecule. Initial measurements were performed with SF_6 in argon, using infrared multiphoton excitation to prepare the vibrational energy distribution of SF_6.

Support by the National Science Foundation and the Petroleum Research Fund is gratfully acknowledged.

4C

EXCITATION AND QUENCHING OF $N_2(B^3\Pi_G)$ IN ELECTRON-IRRADIATED NITROGEN

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Relative efficiencies for exciting vibrational levels of the $B^3\Pi_g$ and the $C^3\Pi_u$ states of N_2 and the $B^2\Pi_u^+$ state of N_2^+ by the electron-irradiation of N_2 have been measured. The distributions over vibrational levels for these states have been determined over a range of pressures to distinguish between population of $B^3\Pi_g$ state vibrational levels by direct electron impact and by collisional and radiative transfer of excitation. The present experimental results agree with previous laboratory measurements, auroral observations, and a kinetic model of the coupled system of the A, B, C and W states of N_2.

These measurements were made by observing the fluorescent intensities of the First Negative band of N_2^+ and the First and Second Positive bands of N_2 in the 1 m dia. Air Force Geophysics Laboratory's LABCEDE vacuum chamber in which N_2 at pressures of 0.15-81.5 mTorr was irradiated by up to 14 mA currents of 4.5 keV electrons. The fluorescence was observed using a monochromator and photomultiplier tube operated to minimize the diffusion of radiators out of the field of view of the detector. The vibrational distributions obtained for the N_2^+ B state and the N_2 C state were invariant over the pressure range used, agreed with the Franck-Condon distributions for excitation of ground state N_2, and agreed with auroral observations. For the N_2 B state, the vibrational distribution for levels v=3-9 at low pressures was consistent with Franck-Condon excitation and radiative cascade production of the B state, and agreed with high altitude auroral observations. As the pressure was increased, the relative populations of levels v=3-9 varied only slightly, also in agreement with auroral observations. A simple kinetic model which included electron-impact excitation and collisional and radiative coupling of the N_2 A, B, C, and W states was developed and found to be consistent with the measurements.

Although electron [illegible] N_2 produces similar N_2 B and W state populations, and [illegible] the W state is tightly collisionally coupled to the nearly [illegible] of the B state, this collisional coupling does not [illegible] the vibrational level distribution for the N_2 B state [illegible] under collisionless conditions. As a result, the [illegible] the W and B states is not responsible for the [illegible] border for a deeply penetrating aurora. However, [illegible] of the W state may have a substantial effect on the infrared spectrum of the aurora.

This work was supported by the U. S. Air Force Office of Scientific Research and the Defense Nuclear Agency.

Potential Energy Surface of Phosphine Oxide

5A

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The reactions of H_3PO serve as a prototype for the infrared multiphoton dissociation mechanisms of more general XYZPO compounds, where X, Y, and Z are monovalent ligands. For example, the infrared multiphoton dissociation of dimethyl methyl phosphonate is known to produce PO radicals. Certain of the reactions studied are undoubtedly also important in the combustion of phosphine, PH_3.

Molecular orbital calculations have been carried out on a series of hydrogen isomerization, hydrogen elimination (both atomic and molecular), and hydrogen abstraction reactions of H_3PO. Species considered are H_3PO, H_2POH, H_2PO, HPOH, HPO, POH, and PO, with H and/or H_2 cofragments. Molecular structures are predicted at the Hartree Fock level using the 3-21G basis set. Single point $6\text{-}31G^{**}$ calculations with MP3 perturbation corrections are used for the prediction of reaction energetics and barriers.

5B

MOLECULAR STUDY OF THE HYDROGEN-HYDROGEN EXCITATION COLLISIONS

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We report total cross sections for the excitation reactions

$$H(1s) + H(1s) \rightarrow H(2s,2p) + H(1s)$$

calculated in an impact-parameter formalism, for high collisions energies. The molecular energies are calculated by a configuration-interaction method. The radial couplings between the molecular wavefunctions are evaluated exactly using the method proposed by Macías and Riera (J. Phys. B., 10 861 (1977); 11, 1077 (1978)).

5C

A Numerical Method for the Transformation to Action-Angle Variables

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A simple and economical method based on the adiabatic hypothesis of classical mechanics for the transformation to good action-angle variables in nonseparable multidimensional systems is presented. The utility of this transformation in chemical problems is demonstrated by several applications to intramolecular dynamics.

6A

Coupled Channel Transition Matrix (T-Matrix) Approximation for the Three-Dimensional Atom-Molecule Reactive Scattering. M. S. BOWERS, B. H. CHOI, Univ. of California at Riverside, and K. T. TANG, Pacific Lutheran Univ. -- A three-dimensional coupled channel transition matrix (T-matrix) approximation is presented for the reactive scattering of an atom and a diatomic molecule. In this approximation, both entrance and exit channel wave functions are calculated from the inelastic vibrational and rotational close-coupling approximation. It is found that this method gives more accurate results than the earlier work of Choi et. al.[1] in which only the entrance channel wave function was obtained from the close-coupling approximation. Also, it is similar to the recent work of Schatz et. al.[2] except that in the present formulation the coupled radial wave functions are calculated in a spaced-fixed rather than a body-fixed coordinate system; therefore, parity decoupling in the present method is simpler and more straightforward. The present method allows for the internal states of both the target and product molecule to be dynamically coupled following the motion of the atom, and it has been shown to give quantitatively accurate reactive cross sections in the threshold region of the $H+H_2$ reaction.[1,2] Thus, this approach provides an excellent means for studying isotopic effects on thermal rate constants. The formulation of the approach, computational procedures, and some numerical results are presented for an asymmetric, isotopic analog of the hydrogen exchange reaction.

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6B

Reduced dimensionality quantum calculations of reaction probabilities: $O(^3)+H_2$, D_2, HD, $\mu+H_2$ and $H+H_2$[a]

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Reduced dimensionality reaction probablities have been calculated for $O(^3)+H_2$, D_2, and HD, using an *ab initio* potential surface. Rate constants and comparisons with experiment will be presented. Calculations have also been done for the $\mu+H_2$ and $H+H_2$ reactions using the LSTH potential surface. The probabilites for these reactions compare very well with recent coupled states calculations of Schatz.

---

[a] This work was supported in part by the Department of Energy, Office of Basic Energy Sciences (DOEDE-AC02-91ER10900). The calculations were done on the IIT Chemistry Department VAX 11/750 computer which was funded in part by the National Science Foundation (CHE-8306272) and the Camille and Henry Dreyfus Foundation.

6C

QUANTUM RESONANCES IN H+CO[a]

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Large scale coupled channel calculations were performed for the H+CO system, using an **ab initio** potential energy surface, over a range of energies where complex formation is possible. We report the existence of several resonances for zero total angular momentum and treating CO as a rigid-rotor. This is the first report of quantal scattering resonances in a three-dimensional, strongly chemically interacting system which can form a stable adduct. Thus, unlike van der Waals systems, the present system offers a realistic opportunity to test statistical theories of scattering and recombination, e.g., RRKM theory and the statistical adiabatic channel model. These resonances could conceivably be observed experimentally.

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[a] This work was supported in part by the Department of Energy, Office of Basic Energy Sciences (DOEDE-AC02-91ER10900). The calculations were done on the IIT Chemistry Department VAX 11/750 computer which was funded in part by the National Science Foundation (CHE-8306272) and the Camille and Henry Dreyfus Foundation.

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[c] Supported by the Department of Energy under contract W-31-1-9-Eng-38

7A

A semiclassical calculation of the temperature dependence of inelastic phonon transitions in gas-surface scattering: He/Si(100)-(2X1) [a)]

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ABSTRACT

Inelastic atom-surface phonon scattering for a model He/Si(100)-(2X1) system is investigated by the classical trajectory quantum-forced oscillator **DECENT** method. All one- and two-phonon creation and annihilation intensities are presented for surface temperatures of 100, 300 and 600 K and the time-of-flight spectra are simulated for these three temperatures. The contribution of one- , two- and multi-phonon events to the total energy transfer between 0 and 600 K is also given.

a). Support from the National Science Foundation (CHE-811784) is greatefully acknowledged.

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PHOTOPREDISSOCIATION OF VAN DER WAALS DIMERS IN THE GROUND ELECTRONIC STATE

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The first experiments on Van der Waals dimers infrared predissociation exhibited fairly large linewidths which correspond to very fast energy redistribution or dissociation.In more recent experiments,fine structure corresponding to relatively long lifetimes have also been reported. The internal energy distribution of the dissociation products is a clue for understanding the mechanism of such a half-collision.

The infrared absorption spectrum of the ν_4 band of $(NO)_2$ has been recorded at 0.3 cm^{-1} resolution in a cell cooled down to 110 K.From the band contour analysis and comparison with a simulated spectrum, accurate values of the rotational constants in the ν_4 state are derived, showing a reduction of the Van der Waals bond on vibrational excitation. A lower limit of the time for energy redistribution of 50 to 100 ps is proposed.

The infrared photopredissociation of $(NO)_2$ has been directly observed in a crossed laser molecular beam experiment using bolometric detection of the beam attenuation. An upper limit of the dissociation lifetime can be set to 10^{-3} second.

Investigation of the internal energy of the fragments is in progress,using a Raman-shifted Nd-YAG pumped dye laser as a tunable infrared source and LIF detection.

Reference: Ph.Bréchignac, S.DeBenedictis, N.Halberstadt, B.J.Whitaker and S.Avrillier,J.Chem.Phys.,to be published.

7C

ROTATIONAL INELASTIC CROSS-SECTIONS FOR MOLECULES OF ASTROPHYSICAL INTEREST (OCS AND NH_3) : a comparison between theory and experiment.

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The study of absorption lineshapes in the infrared region(5μm) by means of a diode laser spectrometer allowed us to determine the pressure broadening cross-sections as a fonction of the rotational quantum number J for the systems OCS-Ar,OCS-He and OCS-H_2 . By applying the results of the Sudden approximation, comparison of the experimental results with the theoretical values enabled an estimation of the quality of the intermolecular potentials used to be made .

The parallel study in the $\nu_3 + \nu_2 - \nu_2$ band at 5μm of OCS showed clear evidence,for the first time,of infrared collisional narrowing in the very simple four-level system at moderate pressure . The semi-classical calculations showed that the intra doublet inelastic rate (ε) is very sensitive to the details of the potential.

Therefore we have shown at the same time an experimental method and a theoretical model which allow us to access two types of information: the pressure broadening coefficient (γ) and the intra doublet inelastic rate.

A similar study on ammonia perturbed by H_2 at room and at low temperature allowed us to determine a broadening cross-section and also the intra doublet inelastic rate (due to molecular inversion) .

8A

ENERGY LOSS SCALING FOR SMALL ANGLE ROTATIONALLY INELASTIC SCATTERING

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We consider small angle, rotationally inelastic collisions between an atom or atomic ion and an initially non-rotating diatomic molecule at collision energies from a few eV to several hundred eV. In this region we have used classical perturbation scattering theory to claculate translation-rotation energy transfer.[2] We found that for scattering at a particular reduced deflection angle $\tau = E\Theta$, where E is the initial relative translational energy and Θ the center of mass scattering angle, the energy transferred into rotation scales with the collision energy

$$E\Delta E_{rot} = f(\tau). \qquad (1)$$

Here $f(\tau)$ is a complicated function dependent on the atom (ion)-diatomic potential and the collision masses. Formulas and prescriptions for calculation can be found in ref. 2.

We have verified this result using full classical trajectories. A model Li^+-CO potential surface was constructed and classical trajectories were run over the surface at a translation energy of 2.4 eV and 4.8 eV. If the scaling relationship of eq. (1) is true, we would expect $E\Delta E_{rot}$ to be the same for various combinations of E and Θ whose product is a particular value of τ. This was indeed found to be the case.

We will discuss the intuitive reasonableness of this result and other similar scaling laws.

A short report of this work has already been published in ref. 1.

This research was supported by the National Science Council of the Republic of China.

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TWO-PHOTON RESONANT THIRD HARMONIC GENERATION REFLECTING INTERNAL STATE POPULATIONS IN CW CO FREE JETS

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Harmonic generation and frequency mixing are well established techniques for extending the visible laser range by frequency conversion through different kinds of nonlinear media : (1) crystals currently used, but optically opaque below about 195 nm, (2) gaseous media in cells (rare gases, metal vapors, H_2, CO) with windows of limited spectral transmittance, or differential pumping, (3) pulsed jets providing a windowless environment as proposed and used successfully by Rettner et al.[1] In the present work, we demonstrate the feasibility of third harmonic generation through continuous free jets, as produced at Saclay with a zone of silence.[2] The laser system consists of a Nd:YAG pumped, frequency doubled dye laser (Quantel model YG 481, TDL IV). The VUV radiation is successively extracted using differential pumping, separated from the laser light (fundamental) with a 1 m vacuum monochromator (Mc Pherson model 225), detected by an electron multiplier, and treated by a boxcar integrator (Stanford Research Systems model SR 250).

The third harmonic power P_3, attainable with a laser power P_1 incident on a gaseous medium at frequency ω_1, is such as :[1,3]

$$P_3 \propto \sum_i [N_i \chi_i^{(3)}]^2 P_1^3$$

where i is an internal state of the medium, N_i is the number density for the state i, and $\chi_i^{(3)}$ is the third order nonlinear susceptibility at frequency $3\omega_1$, for the state i. The frequency conversion is greatly enhanced by a two-photon resonance via an electronically excited state of the nonlinear medium.[3] Furthermore, the flow cooling in the jet makes it possible to operate at high state density N_i, without increasing the total gas density and, consequently, the absorption phenomena.[4]

In our experiments, frequency tripling (284 → 94.6 nm) is achieved in a c.w. supersonic jet of CO. The two-photon resonance is obtained between the ($X\ ^1\Sigma^+$, v = 0, J") and ($A\ ^1\Pi$, v = 4, J') states. The rotational lines of 5 branches O, P, Q, R, S, corresponding to ΔJ = -2, -1, 0, +1, +2, are observed. These spectra reflect the rotational populations of the ground state ($X\ ^1\Sigma^+$, v = 0) depending on the degree of rotational cooling which increases along the free jet.[4]

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8C

REACTIVE COLLISION $O + H_2 \rightarrow OH + H$ WITH ELECTRONICALLY EXCITED STATES IN A CROSSED BEAM EXPERIMENT

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Electronically excited state channels in a reacting triatomic system are of fundamental interest, but difficult to investigate in crossed beam experiments, due to the lack of kinetic energy for crossing the encountered thresholds or activation barriers. The system $O + H_2$ is studied in the channels :

$$O(^3P) + H_2(X^1\Sigma_g, v) \rightarrow OH(X^2\Pi) + H \quad (1)$$

$$O(^1D) + H_2(X^1\Sigma_g, v) \rightarrow OH(X^2\Pi) + H \quad (2)$$

$$\rightarrow OH(A^2\Sigma^+) + H \quad (3)$$

Reaction (2) is exothermic, while reactions (1) and (3) are possible only if an additional energy is provided, for instance by vibrationally exciting H_2 at least up to $v = 1$ for reaction (1) and $v = 5$ for reaction (3).

The reactive scattering experiment is performed by crossing O and H_2 supersonic molecular beams skimmed from free jet zones of silence.[1] The dissociation of O_2 is produced by radiofrequency discharge (22 MHz) in the reservoir of a quartz nozzle with an efficiency of 50 to 80 %, yielding $O(^3P)$ alone in Ar, or $O(^1D,^3P)$ in He seeded mixtures, respectively.[2] The vibrational excitation of H_2 is obtained by radiative decay from electronic states (excited in the H_2 beam by means of a coaxial low energy electron beam) to the vibrational levels of the ground state. The final distributions are well predicted theoretically.[3]

In the experiment currently under way, reaction (3) has been observed by detecting the overall spontaneous fluorescence signal from $OH(A^2\Sigma^+)$ emitted from the collision zone. The spectral analysis of this fluorescence is now in preparation. Also, time-of-flight spectra of $OH(X^2\Pi)$, resulting from reaction (1), have been obtained on the axis of the oxygen beam ($\theta = 0°$).

A complete set of potential energy surfaces has been calculated by X. Chapuisat and G. Durand at Orsay, for the same reactive systems.[4]

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9A

MOLECULAR BEAM REACTIONS OF ORIENTED MOLECULES. Howard S. Carman, Jr.*, Philip R. Brooks, Peter W. Harland**, Department of Chemistry, Rice University, Houston, TX 77251.

The orientation dependence of the reaction $K+CF_3Br \rightarrow KBr+CF_3$ has been studied using the crossed molecular beam technique. A supersonic beam of CF_3Br is state-selected using a hexapole electric field and then oriented in the laboratory. The beam of oriented molecules is then crossed with a thermal beam of K atoms. The laboratory angular distribution of reactively scattered KBr is measured with a differential surface ionization detector for different relative orientations of the reactants. Reactions at different "ends" of the molecule result in markedly different angular distributions, with the Br "end" giving backward scattering in the center of mass with a much greater reactive cross section than the CF_3 "end" which gives forward scattering. The results are qualitatively consistent with an electron-transfer "harpoon" mechanism which was used to explain the reactive scattering of the $K+CF_3I$ system (1). There are differences, however, in the results of the two systems, possibly indicating a more complicated orientation dependence for the $K+CF_3Br$ reaction. The recent experimental results for CF_3Br will be presented and contrasted with the earlier, more extensive, CF_3I results.

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9B

The Effect of Intramolecular Coupling in Malonaldehyde via a Synthesis of the Reaction Surface Hamiltonian and the Kinetic Coupling Model

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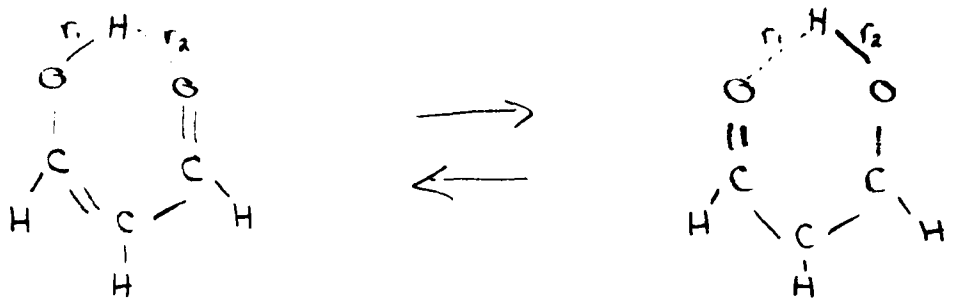
The intramolecular hydrogen atom transfer in malonaldehyde involves two strongly coupled anharmonic degrees of freedom.



The dynamics is not dominated by motion along a one-dimensional path and a reaction path treatment is insufficient. Rather than approximating the potential energy surface by a multi-dimensional harmonic valley about a one-dimensional path it is better to approximate it with a harmonic expansion about a two-dimensional surface. The potential is more accurately represented by assuming that it is quadratic in displacements of internal coordinates from their values on the reaction surface (the two-dimensional analogue of the reaction path) than by assuming that it is quadratic in Cartesian displacements. The Hamiltonian is written in terms of two coordinates r_1 and r_2 which specify the location of a point on the two-dimensional reaction surface, Q_k local normal mode coordinates, and their conjugate momenta. The normal mode coordinates are linear combinations of displacements of internal coordinates from their values on the reaction surface chosen so that they represent motion orthogonal to the reaction surface. This internal coordinate version of the reaction surface Hamiltonian (J.C.P. 81 3942 (1984)) combines advantages of the reaction surface idea and the kinetic coupling model (used for example by Sibert et.al., J.P.C. 87 2032 (1983) and J.C.P. 81 1115 (1984)).

9C

Theory of Multiphoton Excitation of Methane in Intense Laser Fields

by

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Abstract

The quantum dynamics of methane in an intense laser field is investigated through the time dependence of band transition probabilities, photon number absorption, and their long-time-averaged analogs. A local mode Hamiltonian is used to describe the stretch vibrational spectrum of methane, and this "ladder" of stretch states is shown to be inefficient for state-resonant excitation because of a vibrational bottleneck. Enhancement of multiphoton excitation due to rotational motion is demonstrated. Novel methods from artificial intelligence are implemented in conjunction with the Recursive Residue Generation Method[1] to treat this large basis size problem.

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10A

Conformational Kinetics of Methyl Nitrite Collisional Energy Transfer in the Bimolecular Region

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Pressure dependent bimolecular region unimolecular rate constants for the syn-anti conformer exchange in gaseous methyl nitrite and in methyl nitrite bath gas (He, Ne, Ar, H_2, N_2, O_2, CO, CO_2, NH_3, SF_6, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, and n-C_5H_{12}) mixtures were obtained from lineshape analysis of 200 MHz ^1H NMR spectra. The pressure dependent rate constants were analyzed to yield relative bimolecular region collisional activation efficiencies. The resulting efficiencies indicate that, for methyl nitrite conformer exchange (E_0=11.7(0.4) Kcal/mol, $\rho(E_0)$=160 states/cm^{-1}), which is a reaction that appears to follow RRKM kinetics, the intermolecular energy transfer is dominated by the attractive portion of the intermolecular potential, with the intermolecular vibrational energy transfer being statistical.

Additional studies in the bimolecular region have provided information about the bimolecular region Arrhenius activation energy and the threshold energy to reaction (E_a=11.2(0.2) Kcal/mol, E_0=11.7(0.4) Kcal/mol). At pressures below ca. 15 torr, the reversible nature of the reaction allows for multiple reactions of energized molecules, resulting in deviations from the RRKM predicted falloff.

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10B

Laser-Assisted Charge-Transfer Reactions (Li^{3+} + H):

Coupled Dressed-Quasimolecular-State Approach

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A semiclassical coupled dressed-quasimolecular-states (DQMS) approach [1,2] is presented for nonperturbative treatment of multichannel charge-transfer reactions at low collision velocities and high laser intensities, incorporating the implementation of the generalized Van Vleck (GVV) nearly degenerate perturbation theory [2]. The GVV technique allows block partitioning of the infinite-dimensional Floquet Hamiltonian into a finite-dimensional model DQMS space, and thereby reduces greatly the number of effective coupled channels. Further, the GVV-Floquet basis allows minimization of the (usually large in amplitude) field-induced nonadiabatic radial couplings without the need to explicitly construct the transformation between the adiabatic and diabatic DQMS basis. This yields a new set of coupled GVV-DQMS equations (neither adiabatic nor diabatic) which are particularly convenient for multichannel calculations [2]. The method is applied to the study of the laser-assisted charge-transfer process: $Li^{3+} + H(1s) + \hbar\omega \rightarrow Li^{2+}(n=3) + H^{+}$, using 2-, 5-, and 15-GVV-DQMS basis. It is found that while the 5-state results agree well with the 15-state calculations even up to very high intensities for the $(LiH)^{3+}$ system, the 2-state basis is inadequate at high-intensity and lower-wavelength regimes. Detailed results and nonlinear dynamical features are presented [2] for the process at small impact velocity 10^7 cm/s and strong laser fields with intensity ranging from 1 to 100 TW/cm^2 and wavelengths from 1500 to 3000 Å.

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10 C

1985 Conference on the Dynamics of Molecular Collisions, Snowbird, Utah, July 14-19

CLASSICAL MECHANICAL SIMULATION OF ROTATIONALLY INELASTIC COLLISIONS

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A classical trajectory code was completely restructured to allow for efficient vectorization on a Cray-1 supercomputer. This code was used to calculate the rotational energy transfer rate constants for collisions of rotationally excited CO, with initial rotational quantum number j=10 or 20, and Ar.[1] The poster presentation will include a discussion of vectorization techniques for classical trajectory calculations. In future work the converged classical rates will be compared to quantal calculations employing a sudden approximation and used to test scaling relations based on the energy-corrected sudden approximation.[2]

This work was supported in part by the National Science Foundation and the University of Minnesota Supercomputer Institute.

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11A

ROTATIONAL-STATE-SPECIFIC ENERGY TRANSFER IN OH AND OD

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Rate constants k_Q for collisional quenching of $A^2\Sigma^+$, v'=0 OH and OD have been measured for specific rotational levels N' of the radical and a wide variety of collision partners. Measurements were made of the time-dependent laser-induced fluorescence signal in a low pressure discharge flow at room temperature. We observe a decrease in k_Q with increasing rotational quantum number[1] for most quenchers.[2] The internal levels of the collision pairs appear unimportant from experiments involving deuterium substitution. A comparison of rotationless rates for different colliders, $k_Q(N=0)$, with calculations based on collision complex formation indicate that attractive forces play a role in the quenching process.

Preliminary infrared-ultraviolet laser double resonance experiments have been performed on the ground state of OH. Transfer between neighboring λ-doublet components and a strong propensity for retention of the λ-doublet component during rotational transfer have been observed for collisions of $OH(X^2\Pi, v=2)$ with H_2O.[3]

Support: National Aeronautics and Space Administration under contract NAS1-16956.

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11B

Propensity Rules in Collisions of Open-Shell Molecules: Novel Quantum and Classical-Limit Studies*

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Over the past decade there have been a number of articles devoted to the development of the quantum theory of collisions involving open-shell molecules. Energy transfer in these systems has a richness not seen in closed-shell systems, due to the multiplet structure of the rotational levels which arises from the coupling between the rotational motion of the molecule and the spin and/or electronic orbital angular momentum of the unpaired electrons. One of the most exciting advances in this area has been the development of general collisional propensity rules governing the relative magnitudes of cross sections for transitions between these various multiplet levels. The validity of these propensity rules is independent of the interaction potential of the particular system in question.

In our previous work, the development of these propensity rules has depended on the use of the Infinite-Order-Sudden limit to the quantum close-coupled equations. We shall show, using a vector recoupling of the various angular momenta which play a role, that a more general derivation can be made, which is independent of any dynamical approximations. In doing so, we make use of a new expansion of the cross sections in terms of tensor opacities which are independent of the electronic spin. These tensor opacities are proportional to the probability for reorientation of the nuclear rotational angular momentum during the collision. This will also allow us to predict the expected strength of these propensity rules for several physically reasonable models for the tensor opacities.

Another result of the present theoretical work is the development of classical limit techniques for the study of open-shell systems. This will allow conventional classical trajectory techniques to be used to study energy transfer in open-shell systems, without neglecting the quantum mechanical degrees of freedom imposed by the unpaired electrons. The key lies in the calculation of the spin-independent tensor opacities by standard trajectory techniques, while using conventional angular momentum algebra to fully account for the electronic spin degrees of freedom, which introduce a purely geometrical, nondynamical effect.

* Research supported by the National Science Foundation, Grant CHE84-08528 and by the U. S. Army Research Office, Grants DAAG29-84-G-0078 and DAAK29-85-K-0018.

DYNAMICS OF THE REACTIONS C + NO AND C + N_2O. 11C

EXPERIMENTS WITH CROSSED PULSED MOLECULAR BEAMS AND THEORETICAL APPROACH

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The dynamics of the C + NO → CN + O and C + N_2O → CN + NO reactions are reinvestigated using pulsed supersonic crossed molecular beams. Atomic carbon seeded in a supersonic expansion of argon is produced by laser vaporisation of graphite. CN radicals are probed by the laser induced fluorescence technique. The energy partitioning into the CN product is determined for various kinetic energies of the reactants. These results are compared with those of classical trajectories made on analytic potential energy surfaces fitted from quantum mechanical calculations.

12 A

HIGH KINETIC ENERGY (1-5eV) LASER SUSTAINED NEUTRAL ATOM BEAM SOURCE

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Development of high energy (1-5eV) neutral atom beams has relied primarily upon the use of charge exchange or DC/RF discharge techniques. We will describe the use of laser sustained plasma technique for producing high intensity ($>10^{15}/cm^2$-s) and high translational velocity (>4km/s) atomic beam species for use in gas-surface scattering experiments. Laser sustained plasmas have demonstrated temperatures of 12,000 K in xenon and 30,000 K in helium and when coupled with hydrodynamic expansion techniques will be capable of producing molecular beam velocities greater than 10 km/s for a wide variety of species. Initial experiments with xenon using 70 watts of CO_2 laser power have demonstrated beam kinetic temperatures of 8-9,000 K with Mach numbers of 4-5 resulting in peak velocities of 1.5km/s. Extrapolation of these results to helium predicts that velocities in excess of 10 km/s are possible but will require the use of 1-2 kW of CO_2 laser power. Experiments performed with a 1/2 kW CO_2 laser will be described.

A Discrete Sudden Perturbation Theory for Inelastic Scattering

12 B

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The infinite-order sudden (IOS) approximation has long been popular because of its great simplicity and speed. However, it is not very accurate in many cases. A perturbation theory based on the IOS is difficult because one of the perturbations is a change in energy which persists out to $R=\infty$ and thus causes an infinite result. In the present work this difficulty has been circumvented by using a double perturbation theory. First, the elastic contribution due to the spherically averaged potential is removed. The radial wave functions are expressed in terms of the well-behaved and the singular, solutions for elastic scattering. and a set of equations are obtained for the coefficients. This removes the rapid oscillations from the scattering matrix due to the elastic phase shift. Next the equations are transformed to the IOS representation in two steps. First they are transformed from the space-fixed representation to the body-fixed representation, nearly diagonalizing the orbital angular momentum. Then, the internal quantum numbers are approximately diagonalized using the discrete variable transformation of Parker, Lill, and Light. This same set of operations can be done for the IOS approximation to yield a set of diagonal equations which are easily solved. Finally, the true coefficients are expressed in terms of the IOS values to yield a perturbation on the IOS. The equations converge very nicely. Because the perturbation is small, they can be solved accurately by an exponential perturbation theory. Calculations for $Ar+N_2$ are are very much more accurate than either the IOS or a straight exponential perturbation theory.

The quantal theory has been made into a variation on the exponential time-dependent perturbation theory. Here again, only the perturbation on the IOS is treated as an approximation. In this case, however, the perturbation is calculated as an integral on a classical trajectory, and this requires much less computer time than the fully quantal calculation.

12C

Collision-Induced Transitions between Molecular Hyperfine Levels: Quantum Formalism, Propensity Rules, and Experimental Study of $CaBr(X^2\Sigma^+)$ - Ar

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As an extension of our previous theoretical[1] and experimental[2,3] work on collision-induced transitions between rotational and fine-structure levels in open-shell molecules, we present here the general treatment of collisions of a molecule with hyperfine structure. We also show that in hyperfine-resolved collisional transitions the propensity rule $\Delta F = \Delta J$ should be obeyed, as is well known for radiative transitions. Use is made of the recoupling technique recently employed by Corey and McCourt[4] to allow the $F \rightarrow F'$ sections to be expressed in terms of spin-free tensor opacities.

In addition, we also report the first experimental study of hyperfine-resolved inelastic cross sections involving a molecular species, namely collisions of $CaBr(X^2\Sigma^+)$ with argon. This is an extension of our previous studies[2,3] of $CaCl(X^2\Sigma^+)$ collisions without resolution of hyperfine level. Here, we take advantage of the fact that CaBr has resolved hyperfine structure in its electronic spectrum and that an electric quadrupole state selector selectively refocuses different hyperfine levels.[5] The relative final hyperfine level populations have been determined for several collisional transitions. These results clearly display the $\Delta F = \Delta J$ propensity rule and disagree with the M_J-randomization model, which predicts a statistical F' distribution. The experimental relative F' populations agree nearly quantitatively with a simulation of the experiment using the previously determined[3] $CaCl(X^2\Sigma^+)$ - Ar tensor opacities.

This work has been supported in part by the National Science Foundation under grant CHE-8405828.

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13A

ADIABATIC APPROACH TO POLYATOMIC PHOTODISSOCIATION: APPLICATION TO C_2N_2*

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Recent experimental studies indicate that C_2N_2 undergoes indirect photodissociation between 164 and 158 nm proceeding via

$$C_2N_2(\tilde{X}\ ^1\Sigma_g^+) + h\nu \rightarrow C_2N_2(\tilde{C}\ ^1\Pi_u) \rightarrow CN(X\ ^2\Sigma^+) + CN(A\ ^2\Pi) \qquad (1)$$

Fragment vibrational distributions have been reported for several wavelengths.[1,2] A main goal of the present theoretical effort is the evaluation of these distributions.

An adiabatic approach has been developed[3,4] which enables process (1) to be treated as a quantum transition in which the fragment distributions are evaluated in a golden rule formalism. The method explicitly treats the coupling between the relative and internal motion of the fragments. The vibrational frequencies and equilibrium bond lengths of the fragments are found to depend on the interfragment distance.

The theory has been applied to the collinear predissociation of $C_2N_2(\tilde{C}\ ^1\Pi_u)$. Ab initio minimum basis set multiconfiguration Hartree-Fock (MCHF) calculations were performed to obtain molecular geometries, vibrational frequencies, and force constants of the $\tilde{C}\ ^1\Pi_u$ quasidiscrete state and the CN fragments.

Computed vibrational distributions of the photofragments will be reported and compared to experiment. The validity of the approximations used and the sensitivity of results to the ab initio data will be discussed.

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*This work was supported by the Director, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
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13B

Abstract: For the 1985 conference on the Dynamics of Molecular Collisions, Snowbird, Utah. July 14-19, 1985.

A MODEL FOR THE REACTIONS OF NON-METAL ATOMS.

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The rates for the gas phase reactions of non-metal atoms with simple molecules measured in several laboratories (including ours) display puzzling patterns. For example, Boron and the group IV elements C, Si, Ge and Sn all react readily with O_2. Reaction cross sections are close to gas kinetic. Of these atoms C, Si and Ge react also with N_2O, but the reactivity of B and Sn with N_2O is a thousand times smaller. Furthermore, in the case of B and Sn a large fraction of the reactions that do occur produce electronically excited oxide molecules. A model is presented which provides a qualitative explanation for these as well as several other observations. The model suggests that hindrances in the entrance as well as in the exit channels of the reaction are produced by the local electron density distributions. The basic features of the model are substantiated by MNDO computer calculations of the parameters relevant to the reacting systems.

13C

BOTTLENECKS TO INTRAMOLECULAR ENERGY TRANSFER AND THE CALCULATION OF RELAXATION RATES*

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A recently developed theory of MacKay, Meiss, and Percival [Physica D **13**, 55 (1984)] and Bensimon and Kadanoff [Physica D **13**, 82 (1984)] is applied to the intramolecular relaxation of highly excited, collinear OCS. This theory, which was originally developed to understand the long time relaxation of mappings, possesses many of the features of statistical theories of reactions. Bottlenecks, dividing surfaces, and transition states are all part of the theory, which we employ here to describe the relaxation dynamics of collinear OCS. In particular, the theory is used to find a bottleneck to intramolecular energy transfer, generate a dividing surface, derive the flux across this dividing surface, and then calculate the rate across it. A simple kinetic model then employs this rate to accurately predict the rate of relaxation for collinear OCS. At present the theory is purely classical mechanical, has only been applied to systems of two degrees of freedom, and has only been used to describe the dynamics of bound systems. We discuss extensions of the theory in these three areas.

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Dissociation on Solid Surfaces: H_2-Ni

14A

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A theoretical treatment of the dissociation of small molecules on metal surfaces requires: 1. a physically correct description of the interaction potential for all arrangements, and an easily computed form for such a potential; 2. a non-perturbative description of the motion of the molecule and a small number of primary surface and sub-surface atoms, and a consistent coupling of the primary atoms to the remaining solid atoms.

We present a many-body expansion[1] of the gas atom-solid surface interaction potential that provides an accurate PES in which the atom-solid atom distances are the only independent variables. This yields a flexible PES form which can be transferred among different surface faces simply by changing the positions of the solid atoms. Symbolically, we have

$$v_{AM}(\vec{x}_A,\underline{y}) = \sum_i v_{AM}^{(2)}(|\vec{x}_A-\vec{y}_i|) + \sum_{i>j}\sum v_{AM}^{(3)}(|\vec{x}_A-\vec{y}_i|,|\vec{x}_A-\vec{y}_j|) + \cdots$$

where $\vec{x}_A$ and $\underline{y}=\{\vec{y}_i,\ i=1,\cdots N\}$ are the positions of the gas atom and the N solid atoms, respectively, and the two and three body interactions are $v^{(2)}$ and $v^{(3)}$. From the atom-surface interactions A•••M and B•••M, we determine the molecule-surface interaction, A-B•••M using the modified 4-center LEPS form[2],

$$V(\vec{x}_A,\vec{x}_B,\underline{y}) = Q_{AB} + Q_{AM} + Q_{BM} - (J_{AB}(J_{AB} - J_{AM} - J_{BM}) + (J_{AM} + J_{BM})^2]^{1/2}$$

where Q and J are couloumb and exchange integrals. These are given in terms of the attractive and repulsive portions of the appropriate interactions by

$$Q + J = V = v(\text{repulsive}) - v(\text{attractive})$$

$$Q - J = (v(\text{repulsive}) + v(\text{attractive}))\ (1-\Delta)/2(1+\Delta)$$

where Δ is the Sato parameter.

An illustration of this many body expansion method is presented for H_2-Ni(100) where the potential parameters are determined from input data on chemisorbed H-Ni(100) and physisorbed H_2-Ni(100)[3]. Two body morse potentials and three and four body exponential forms were used. The dissociation reaction is studied on the Ni(100), Ni(110) and Ni(111) faces using classical trajectory techniques, a 13 atom solid primary zone and $\gtrsim$ 100 secondary atoms. A consistent set of GLE parameters is determined via projection operator analysis of the solid's frequency matrix[4]. Features influencing the variation of reactivity with kinetic energy, internal rovibrational state of H_2 and the exposed surface are discussed.

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14B

On the Solution of the MultiChannel Schrodinger Equation

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Recently, a quasi-numerical technique was developed to determine Magnus-like propagators for the Schrodinger Equation, to high order in the step size. In conjunction with a judicious choice of curve fitting, the derived propagators were successfully applied to a model, single channel problem.[1] (With the same effort, results five orders of magnitude more accurate than the first order Magnus method were obtained.) These propagators have now been applied to a multichannel problem; the results of this application, as well as details of the implementation of the method, will be presented.

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14C

ION MOLECULE REACTIONS INSIDE METHANE CLUSTERS INITIATED BY PHOTOIONISATION

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Ionisation of clusters generated in an supersonic expansion of Ar-CH_4-mixtures leads to a series of ion products, which are formed by reaction of the ionised cluster constituents. The following reaction channels have been observed:

$$(CH_4)_m + h\nu \rightarrow (CH_4)_k^+ + (m-k).CH_4 \quad |1|$$

$$\rightarrow (CH_4)_{k-1}.CH_5^+ + (m-k).CH_4 + CH_3 \quad |2|$$

$$\rightarrow (CH_4)_{k-2}.C_2H_4^+ + (m-k).CH_4 + 2H_2 \quad |3|$$

$$\rightarrow (CH_4)_{k-2}.C_2H_5^+ + (m-k-1).CH_4 + CH_3 \quad |4|$$

$$\rightarrow (CH_4)_k.Ar_l^+ + (m-k).CH_4 + (n-l).Ar \quad |5|$$

$$(CH_4)_m.Ar_n + h\nu \rightarrow (CH_4)_{k-1}.Ar_l.CH_5^+ + (m-k).CH_4 + (n-l).Ar + CH_3 \quad |6|$$

Photoionisation efficiency curves have been obtained for a number of different products and threshold energies for the different reactions have been extracted from these data.

When comparing these results with the dynamics of the analogous ion molecule reactions it is found that reaction |3| is not observed at all in the gas phase while reaction |4| appears at a much lower threshold for $k>3$. This is probably due to the cage effect of the remaining molecules in the cluster. Futhermore it can be shown that reactions inside mixed clusters, |5| and |6|, will proceed via two different channels, each proceeding via the ionisation of the CH_4 and the Ar constituents of the cluster, respectivly.

A number of binding energies for different cluster ions have been deduced from the photoionisation efficiency curves.

A PHOTOION-PHOTOELECTRON-COINCIDENCE METHOD FOR THE INVESTIGATION OF VAN-DER-WAALS CLUSTERS

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Photoionisation experiments have been performed to investigate atomic and molecular clusters. A photoion-photoelectron-coincidence technique has been used to obtain time-of-flight mass spectra:
Monochromatized light from a synchrotron source (Berlin Electron Storage Facility BESSY) produces pairs of cluster ions and electrons, which are separated into opposite directions by a weak homogeneous electric field. The electrons are detected by a channeltron electron multiplier generating a short electronic pulse , which serves as the start pulse for a time-of-flight mass spectrometer. Due to the particular design of the extraction field only electrons below a certain energy (between 0.03 and 0.3 eV), determined by the magnitude of the extraction field, are efficiently collected.

Mass spectra of Ar-, Kr , and N_2O-clusters generated in a supersonic expansion from a high pressure nozzle have been taken as a function of photon energy. Only such processes are detected which produce electrons with negligible energy; therefore, the total amount of energy dissipated in the cluster ion corresponds to the photon energy. It is apparent from the experimental data that the measured distributions show distinct maxima which become more prominent when lowering the photon energy (ant therefore the energy dissipated into the cluster ion). Near threshold only a few cluster sizes remain; these depend on the cluster material (N_2O: n=7; Ar,Kr: n=16) and are not identical with previously found magic numbers in cluster ion mass distributions generated with conventional ionisation techniques.

15B

THEORETICAL STUDY OF VIBRATIONAL RELAXATION IN MOLECULE - SURFACE COLLISIONS USING THE DEFORMATION RESONANCE APPROACH

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Vibrational deactivation probabilities for collisions of CO, CO_2 and NO with various surfaces have recently been reported [1]. As possible mechanisms electron-hole pair formation, vibration-to-rotation energy transfer and excitations of phonons are discussed. In order to examine the relative importance of these various channels, a theory is needed which treats all of them consistently and on equal footing. Such an approach is provided by the deformation resonance model [2] in which all degrees of freedom are described quantum mechanically and the Hamiltonian is split into three parts. The localized part describes the gas molecule if it is near to the surface and contains the interaction with the electron-hold pairs and the phonons. The delocalized part describes the gas molecule if it is far from the surface. The interaction term imbeds the localized problem into gas-particle scattering states. This supplies a clear picture of the inelastic collision: The molecule penetrates the surface region and perturbs the electronic and vibrational structure of the surface. The deformation relaxes by phonon emission (or absorption) and electron-hold pair formation. The gas molecule either sticks or is pushed back into the vacuum inelastically. The scattering mechanism is determined by the properties of the deformation resonance. Using the Franck-Condon factors for the phononic, electronic, vibrational and rotational relaxation, the wave function of the deformed state is calculated numerically in a self-consistent way. For the electronic part a previously developed chemisorption model [3] has been used. The calculations, which are of qualitative nature presently, have been performed for CO and NO on silver.

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15C

Interaction potentials for rare gases on flat and stepped transition metal surfaces

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Self-consistent non-perturbative calculations are carried out for interaction potentials of helium and neon with flat and stepped transition metal surfaces.

The metal surface is described by a cluster of about 300 atoms embedded in a jellium model described by Sommerfeld wave functions. This allows for the dispersion of the metal electrons and local electronic effects at the same time. The interaction with the d-electrons is included in a consistent way. For flat surfaces corrugation is found to be approximately proportional to the d-electron charge density. The attractive part of the potential arises largely through the hybridization of the rare gas orbitals with the unoccupied metal states. This interference energy is roughly a factor two larger for neon than for helium, leading to larger corrugations of the neon potentials. Image force effects are found to be important for the corrugation and softness of the neon potentials.

The charge density for the stepped surfaces exhibits oscillations near the step and a pronounced Smoluchowsky effect. Compared to the flat surface case the rare gas binding energies are increased right at the step and decreased further out on the low terrace.

16A

DYNAMICAL ANALYSIS OF THE COMPETITIVE CHANNELS IN THE Cl^-+H_2 REACTIVE COLLISIONS

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At low collision energy the Cl^-+H_2 system gives rise to 4 endothermal channels:

reaction	$HCl + H^-$	(2.91eV)(R)
reactice detachment	$HCl+H+e^-$	(3.66eV)(RD)
simple detachment	$Cl+H_2+e^-$	(3.6eV) (SD)
dissociative detachment	$Cl+H+H+e^-$	(8.1eV) (DD)

A multicoincident detection of e^- and H^- with fast neutrals HCl and Cl issued from crossed beams of fast Cl^- ions and supersonic jet of H_2, allows a dynamical analysis of the competition between simple detachment and reactive processes and between R and RD.

Both R and RD processes give rise to HCl molecules scattered at the same χ angle of 55±10 deg. in the C.M. frame whatever the collision energy is and independantly of the rovibrational excitation (E_{rv}) of HCl molecule.

The Cl atoms are scattered by SD process at χ angles increasing with the E_{rv} of H_2 molecules. For χ angle = 55 deg. the SD process disappears : reactive processes are dominant.

It is deduced that the reactive processes occur for a preferential orientation of the H_2 molecules relative to the Cl^- velocity vector. They can be schematized by a hard sphere sequential impulse model.

In the R process the E_{rv} of HCl is limited to the lowest vibrational levels whereas in the RD process all the levels which are possible energetically are equally populated. This aspect of the competition between R and RD is well accounted for by surface crossing considerations utilizing a transitory autodetaching HCl^- state.

16B

A Quasiclassical Trajectory Study of The $(H_2 + D_2)^+$ System

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Abstract

We have applied the quasiclassical trajectory method to investigate the effect of vibration and translational energy on the reaction dynamics of $H_2^+ + D_2$ and $D_2^+ + H_2$. Two different vibrational states (v^+=0 and 3) of the charged diatom and five different translational energies (E_T = 0.23, 1.1, 2.1, 4.1, and 6.1 eV) are used in this study. Using diatomics-in-molecules potential energy surfaces, the reaction is assumed to be diabatic (no charge hopping) until the reactants are within 8.0 bohrs and then adiabatic. This very simple theoretical description of the reaction gives good agreement with the experimental results.

16C

STATE-SELECTED ION-MOLECULE REACTIONS USING MULTIPHOTON IONIZATION

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Resonant-enhanced multiphoton ionization is well suited for producing state-selected ions in case we choose a Rydberg State as an intermediate state. This is due to the fact that the geometry of the Rydberg State is almost the same with that of the ion state, so the Franck-Condon factor favors the $\Delta v = 0$ transition between the two states. This method has great advantages for the investigation of the dynamics of ion-molecule reactions. We are applying this method for the study of the reactions of vibrationally state-selected ammonia ions with various small neutral molecules.

We produce the ammonia ions (NH_3^+, ND_3^+) by resonant-enhanced 2 + 1 ionization in a pulsed molecular beam of ammonia. Because of the geometrical changes in going from the pyramidal ground state to the planar intermediate state ($\tilde{B}$ or $\tilde{C}'$Rydberg state) and the planar ion state, the ions are produced in highly pure, vibrationally-selected states in the ν_2 unbrella bending mode. The ions are mass selected by a quadrupole mass filter to eliminate minor contaminants such as isotopes and they are focussed into the reaction cell containing the neutral reactant gas. The unreacted primary ions and product ions are mass analyzed by a second quadrupole mass filter and detected by a channel electron multiplier array. The reactions are studied both by changing the vibrational energy of ammonia ion ($v_2 = 0 \sim 7$) and by scanning the collision energy ($0 \sim 50$ eV laboratory kinetic energy). The reactions we are proceeding are $NH_3^+(v_2)/D_2$, $ND_3(v_2)/NH_3$ and $NH_3^+(v_2)/H_2O$. In the reaction of $NH_3^+(v_2) + D_2$, we observed both the deutreum abstraction which produces NH_3D^+ ion and exchange reactions which produces NH_2D^+ ion. At higher collision energy (~ 4 eV of center of mass kinetic energy), the ratio NH_2D^+/NH_3D^+ increases due to the open of another channel. In the reaction of $ND_3^+(v_2) + NH_3$, we observed the hydrogen abstraction reaction (produce ND_3H^+ ion) which was not reported before. We will discuss the vibrational energy dependence of these reactions.

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17A

Effect of Translational and Electronic Energy on the Reactions of the First Row Transition Metal Atomic Ions with H_2, D_2, and HD

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An investigation of the title reactions has been performed by measuring total reaction cross sections as a function of relative kinetic energy using a guided ion beam technique. These relatively simple systems provide an empirical view of how the electronic structure of a transition metal ion influences reactivity, bond strength and reaction mechanism. By modeling the threshold energy dependence of these endothermic ion-molecule reactions we are able to extract bond energies, $D_0^\circ(M^+ - H)$, and observe their periodic trends. No isotope effect, aside from zero point energy differences, is observed for the reactions with H_2 and D_2. However, for the reactions with HD, each transition metal ion exhibits an interesting and different isotope effect. By varying the conditions in the ion source, reactant ions are produced in electronically excited states. The HD isotope effect shows a strong correlation to electron configuration in all cases. Simple molecular orbital concepts are used to explain these results as well as to describe factors which are critical to insertion into an H_2 bond. Supporting evidence from studies of reactions of non-transition metal ions will also be presented.

17B

On the Perturbative Analysis of the Dynamics of Reactive Collisions

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We explore the application of quantum mechanical perturbation theory to the determination of reactive transition probabilities. The very simple problem of particle reflection and transmission at a one dimensional potential barrier, is examined over a wide range of energies and for alternate perturbative schemes. The first scheme is conventional; the second is based on a quasi-adiabatic (QA) description of the dynamics. We find that for a choice of model parameter values, loosely based on the $H+H_2$ system, the first (conventional) scheme provides quantitatively accurate results. However, at higher system masses, the first scheme results are in only moderate agreement with exact results and are highly sensitive to the variation of distortion potential parameters. For the high system mass case, the QA results are in much better agreement with exact. However, the QA results are also highly sensitive to the variation of QA potential parameters. More recent results will also be discussed.

17C

Hydrogen Atom Transfer Reactions of Rare Gas Atomic Ions with H_2, D_2, and HD

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Guided ion beam techniques are used to examine the hydrogen atom transfer reactions of He^+, Ne^+, Kr^+, and Xe^+ with H_2, D_2, and HD. The reaction cross sections are measured from thermal energies up to about 20 eV c.m. We have discussed the reactions of Ar^+ previously.[1]

It is known that He^+ and Ne^+ are unreactive with hydrogen at low energies even though the ground state reactions are very exothermic. As Mahan pointed out,[2] a crossing of the reactant state surface with the repulsive excited state of H_2 prevents access to ground state products. However, these reactions do occur at elevated energies. Our results for the $He^+ + H_2(D_2)$ reactions are in agreement with an earlier report[3] of an energy threshold of about 9 eV. In the previously unstudied reaction of Ne^+, we find nearly identical behavior. In the reactions with HD, the deuteride product is strongly favored in this threshold region for both He^+ and Ne^+.

The translational energy dependence of the state-selected reactions of Kr^+ ($^2P_{1/2}$) and ($^2P_{3/2}$) with isotopic hydrogen molecules is reported for the first time. The J=3/2 ground state has a larger cross section than the J=1/2 state at thermal and low energies, while the J=1/2 state reacts faster at energies above a few electron volts. The intramolecular isotope effect for reaction with HD exhibits several reversals over the energy range of thermal to 15 eV.

The first observation of the hydrogen atom transfer reaction with Xe^+ is reported here. Our experiments show that xenon reacts at collision energies above the thermochemical endothermicity for the lower spin orbit state, but the onset of the reaction at the threshold is slow. The reaction with HD favors production of XeH^+ and shows a peculiar double peak in the excitation function for formation of XeD^+.

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18A

CLASSICAL DYNAMICS OF ACETYLENE AT HIGH VIBRATIONAL STATES

by

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Abramson et al [1] have recently measured the stimulated emission pumping from a vibrationally excited state of acetylene at the energy of 3.5 eV. The observed eigenvalue distribution was found to follow a Wigner type distribution function which is one of the proposed criteria for quantum chaos. At this energy of excitation acetylene can also be isomerized to vinylidene. We have studied the classical dynamics of HCCH by using techniques of non-linear mechanics; power spectra of the dynamical variables, Maximal Lyapunov Characteristic numbers (LCN), and Linearization of the difference equations of motion of two initially adjacent trajectories. The potential energy surface which we employ is that of Halonen, Child and Carter [2] for model II. At the energy of 2.7 eV above the zpe of acetylene we find chaotic trajectories which differ in their maximal LCN. Those trajectories with small LCN can not be isomerized to vinylidene. This chaotic structure of phase space results in a non-RRKM behaviour for the iromerization process. At 4.3 eV of excitation the phase space is mainly covered by one chaotic component.

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APPARENT "SUPER-NATURAL" ABUNDANCE OF ^{13}C

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We have been looking at the terminal distributions of rotational energy in free jets of CO and CO_2 by Fourier Transform Infrared Spectrometry in the emission mode. We take advantage of the fact that vibrational energy in these species does not relax appreciably during the free jet expansion. Consequently, by heating the source gas to temperatures above 600 K or so we can obtain vibrational spectra that show the rotational energy distributions of the molecules after they have reached the collisionless free molecule flow regime. As a general rule these rotational distributions are markedly non-Boltzmann and we have attempted to "explain" them in terms of a competition between Rotation-Rotation (RR) and Rotation-Translation (RT) transfers during the last stages of the expansion. (1,2)

Recently, in an attempt to extend the temperature range of these experiments to lower translational and rotational "temperatures" we have used a corona discharge to excite vibration in the source gas without adding much energy to translational and rotational modes. The resulting terminal rotational distributions are indeed much narrower than when we depend upon thermal excitation. In the case of CO we obtain vibrational excitation up to the 5th level with a Boltzmann distribution of the vibrational energy. The rotational distributions are the same for each level but are non-Boltzmann. In CO_2 the excitation of the asymmetric stretch mode, the one we "see," is pretty much confined to the first level but the combination bands are also present. More interesting is the appearance of a band about 70 cm^{-1} to the red whose intensity is about 15 per cent of that for the asymmetric stretch fundamental. This new band is clearly due to emission from $^{13}CO_2$, whose concentration should be only one per cent of the $^{12}CO_2$ isomer. There would seem to be three possible explanations: (1) The natural abundance of ^{13}C is higher than the handbooks say; (2) We have stumbled upon an extremely effective isotope enrichment effect; (3) the $^{13}CO_2$ isomer is somehow preferentially excited. Only the last of these seems reasonable. We guess that ground-state $^{13}CO_2$ molecules become excited when they encounter excited $^{12}CO_2$ molecules. The excess energy is taken up by rotation in one or both partners. Because the population of high J levels is so low there are very few suitable collision partners for the reverse step so the vibrational energy is effectively trapped in the $^{13}CO_2$. This isomer band did not appear in the spectra of thermally excited molecules because the upper J levels were then much more highly populated so that collision partners were available for the reverse reaction.

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POSITIVE MUON MOLECULAR IONS AND ION-MOLECULE REACTIONS IN THE GAS PHASE

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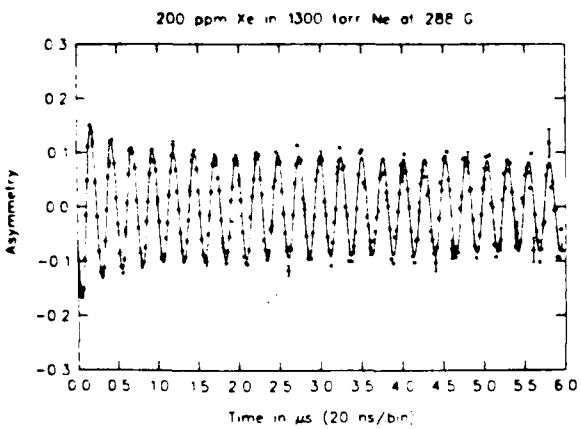
Positive muons thermalizing in gases are found to be in two main environments: diamagnetic, with fraction f_D, or in the paramagnetic muonium atom ($Mu=\mu^+e^-$), with fraction f_{Mu}. These environments are easily distinguished via their μSR signals, in which detected positrons are preferentially emitted along the precessing μ^+ spin direction in a tranverse magnetic field. This signal can be thought of in analogy with free induction decay ($\lambda={}^1/T_2$) in NMR. In noble gas moderators (M=He,Ne,Ar) the diamagnetic environment is due to the formation of μ^+ molecular ions (MMu^+=$HeMu^+$,$NeMu^+$,$ArMu^+$), in like manner to their more familiar protonic cousins (HeH^+, etc.). In pure moderator, the μSR signal due to MMu^+ is very long lived (T_2~50μs) on the 2.2μs time scale of μ^+ decay. However, upon the addition of trace (~100 ppm) amounts of some reagent 'X', a two component relaxation is observed, as exemplified in the Figure for $[NeMu^+]^*$+Xe. We have studied these effects for X=Xe, Kr, NH_3, CH_4, C_2H_4, N_2O and CH_3F in He,Ne and Ar moderators. In general the overall relaxation can be understood in terms of the reaction scheme,



The μSR signal at 288 G in Ne at 1300 Torr with 200 ppm of added Xe. The solid line is a χ^2 fit to the data assuming two different relaxations, giving λ_1 (slow) = 0.044 ± 0.008 μs^{-1} and λ_2 (fast) = 3.18 ± 0.35 μs^{-1}.

$$[MMu^+]^*+X \xrightarrow{k_c} Mu+X^++M$$
$$[MMu^+]^*+X \xrightarrow{k_t} XMu^++M$$

where '*' indicates a (v,J) excited state and k_c and k_t are bimolecular rate constants for thermal charge exchange and muon transfer, respectively. The fast relaxation apparent in the Figure is directly related to k_c but the slow relaxation (λ_1) is not; indeed, k_c/k_t is expected to be or order unity. By measuring the relaxation rate as a function of [X], the bimolecular rate constants k_c can be determined. The results ($10^{-10}ccs^{-1}$) for $[NeMu^+]^*$+X are: Xe(4±1), Kr(7±2), NH_3(26±3), CH_4(≤.02), C_2H_4(20±4), N_2O(11±2) and CH_2F(9±3). Similar values are found for $[HeMu^+]^*$, albeit about 2.5 times larger on average, reflecting the expected change in reduced mass. On the other hand, there is no relaxation seen with $[ArMu^+]^*$ for any X, indicating a more deeply bound vibrational state, likely the result of more efficient quenching collisions with Ar atoms. The lack of any observable fast relaxation with CH_4 (and also C_2H_6) is puzzling and suggests a very fast (perhaps tunneling assisted!) muon transfer reaction such that k_t>>k_c.

AD-A161 070 THE CONFERENCE ON THE DYNAMICS OF MOLECULAR COLLISIONS HELD AT SNOWBIRD U..(U) MINNESOTA UNIV MINNEAPOLIS DEPT OF CHEMISTRY D G TRUHLAR JUL 85 AFOSR-TR-85-0930 2/3

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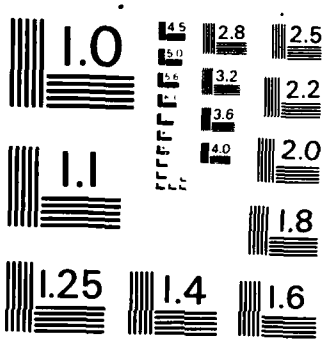

MICROCOPY RESOLUTION TEST CHART
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19A

DRAMATIC ISOTOPIC MASS EFFECTS SEEN IN MUONIUM REACTIVITY:
$Mu+H_2$ and $Mu+C_2H_4$

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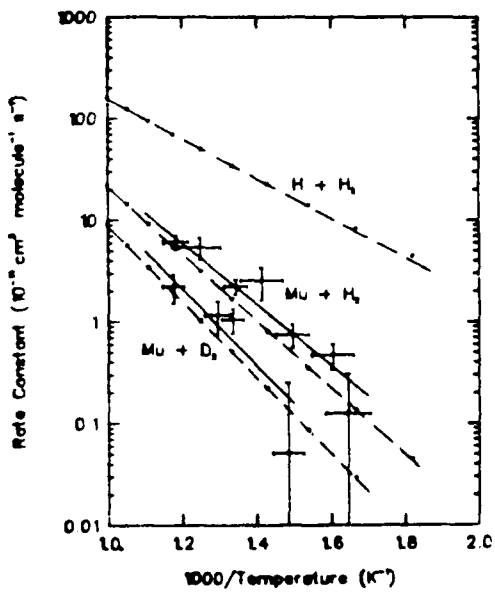
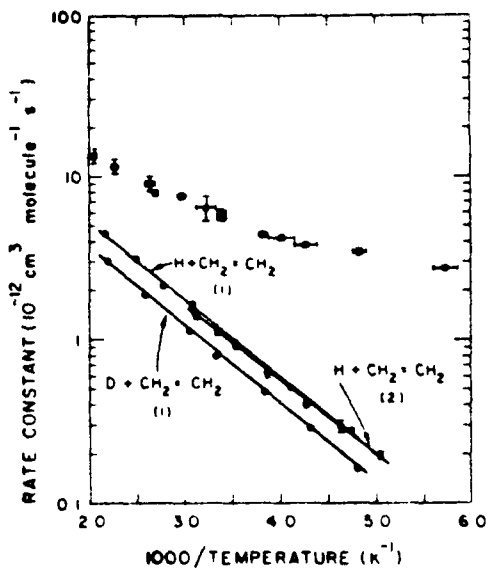
Muonium ($Mu=\mu^+e$), with an ionization potential and size identical to Hydrogen but with a nuclear mass only $^1/_9$th that of H, can be regarded as an extraodinarily light isotope of hydrogen. As such, by studying the thermal rate constants of Mu in comparison with those of the H atom, one can hope to sensitively probe the effects of isotopic mass on reaction dynamics. Two limiting situations can be imagined. Typically in the case of endothermic reactions, the height of the (late) VA barrier is large and quasiclassical effects dominate reactivity with the result that $k_{Mu} \ll k_H$; this is the situation in the $Mu+H_2(D_2)$ reactions. In the other extreme, typified by exothermic reactions with early barriers, quantum tunneling effects can dominate with the result that, at low temperature, $k_{Mu} \gg k_H$; this is the situation in the $Mu+C_2H_4$ reaction. These two reactions are compared and contrasted in the Arrhenius plots of Figures 1 and 2, respectively.





In Fig. 1 (left), the dashed lines are from variational TST calculations carried out by Garrett and Truhlar on the Liu-Siegbahn surface (D.K. Bondi et al., J. Chem. Phys. 76 (1982) 4986). The top line is for $H+H_2$ and, as previewed above, the rate constants k_H are much larger than k_{Mu} over the whole T range (~600-850K) studied. More importantly, at high temperature the theory reproduces the experimental results for both $Mu+H_2$ and $Mu+D_2$ essentially exactly. In Fig. 2 (right), the upper set of data points are for the $Mu+C_2H_4$ reaction, in the T range ~170-500K; note the pronounced break in the Arrhenius plot at ~250K. Such a break is not observed at all in the corresponding $H+C_2H_4$ or $D+C_2H_4$ reaction (K. Sugawara et al., Chem. Phys. Letts. 78 (1981) 259); indeed, at the lowest temperature studied, $k_{Mu}/k_H \sim 30/1$. This is perhaps the most unambiguous example yet of the importance of quantum tunneling in any chemical reaction. On the other hand, at high temperatures, the ratios $k_{Mu}/k_H/k_D$ are just what is expect classically.

19B

MUONIUM HOT ATOM CHEMISTRY IN ALKANE VAPORS

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As part of its thermalization process, muonium with kinetic energies>>k_BT (i.e., "hot") can undergo certain chemical reactions with much larger cross sections than those prevailing at thermal energies. These processes are manifest in the magnitude of the diamagnetic fraction f_D or hot atom "yield" which can be interpreted in terms of a "reactivity integral" I defined in Wolfgang-Estrup theory by

$$I = \int_{E_1}^{E_2} \sigma(E) f(E) dE$$

where $\sigma(E)$ and $f(E)$ are the reactive cross section and distribution function of hot atoms in the energy interval $E_2(\sim 20eV) - E_1(>k_BT)$, respectively. We have compared hot Mu(Mu*) with hot tritium (T*) yields for a variety of alkane (RH) moderators in order to establish the importance of dynamic mass effects in hot atom chemistry. Although we cannot distinguish individual (Mu*H or Mu*R) yields in Mu* chemistry, a disadvantage in comparison with T* chemistry, we can delineate hot atom from thermal reactions, an ambiguity which continues to plague hot tritium work.

The Table presents the hot atom yields for both Mu* and T* with a variety of RH molecules as well as the corresponding reactivity integrals I. This is really the first detailed comparison of the effects of isotopic mass on hot atom reactivity at the most sensitive end of the mass scale - a factor of 27 between Mu and T! In general, the ratio of hot atom yields for T*/Mu* are ~4/1, which translates into a ratio of reactivity integrals $I_{T*}/I_{Mu*} \sim 6/1$. There are no theoretical calculations of hot atom reactivity for the molecules in the Table. Current calculations comparing Mu* and T* reactivity with F_2 [Connor et al., Mol. Phys. 46, 1231 (1982) and work in progress] give only ~2 for the ratio I_{T*}/I_{Mu*}; not surprisingly, inconsistent with the factor of ~6 seen in the present study. It is noted that these ratios are likely to be less sensitive to details of the (unknown) potential energy surfaces than the actual cross sections themselves.

Comparison of Mu* and T* hot atom yields and reactivity integrals in some alkane vapours (RH)

RH	T*(Yield)	Mu*(Yield)	I_{T*}	I_{Mu*}	I_{T*}/I_{Mu*}
CH_4	0.50	0.12	0.70	0.09	7.9
C_2H_6	0.65	0.19	1.5	0.25	6.0
C_3H_8	0.66	0.21	2.1	0.42	5.0
n-C_4H_{10}	0.68	0.21	2.3	0.45	5.1
n-C_5H_{12}	0.69	0.15	~2.4	0.33	~7.3
n-C_6H_{14}	0.72	0.24	~2.5	0.55	~4.5

19C

The Reaction of Spin-Orbit State-Selected $Ca(^3P_J°)$ with Alkyl Bromides

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An optical pumping state selection technique has been employed to study the chemical reactivity of individual $Ca(^3P_J°)$ spin-orbit states. As an extension of our previous study of the Cl_2, Br_2, and CH_3Cl reactions,[1,2] we present here a study of the spin-orbit dependence of the CaBr A and B state chemiluminescence channels for the reaction of $Ca(4s4p\ ^3P_J°)$ with CH_3Br, CH_2Br_2, CH_2CHCH_2Br, and $C_6H_5CH_2Br$. The spin-orbit dependence for the dibromomethane and allyl bromide reactions is substantial, with a reactivity ordering similar to that observed previously with Cl_2 and Br_2, namely J=2 > J=1 > J=0. A weaker spin-orbit dependence was observed for methyl bromide and benzyl bromide.

One complication in these experiments is the presence of the additional metastable state $Ca(4s3d\ ^1D)$, which also reacts to form excited CaBr. Because of a revised smaller theoretical $Ca(^1D-^1S)$ radiative transition rate[3], the $^1D/^3P°$ ratio in the beam is now believed to be approximately 25%. An attempt will be made to gauge the importance of the ^1D reaction by optical pumping experiments in which ^1D atoms will be removed by excitation of the $4s5p\ ^1P° \leftarrow 4s3d\ ^1D$ line near 672 nm. Chemiluminescence, total attenuation, and nonreactive intramultiplet mixing cross sections have also been determined from the pressure dependence of the chemiluminescence and $Ca(^3P_1° \rightarrow ^1S)$ emission intensity.

This work has been supported in part by the National Science Foundation under grant CHE-8400014 and the U.S. Army Research Office under grant DAAG29-85-K-0018.

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20 A

OBSERVATION OF COLLISION-ENERGY, PRODUCT-STATE, AND ANGULAR-SCATTERING SPECIFICITY IN THE CHARGE-TRANSFER REACTION OF $Ar^+(^2P_{3/2})$ WITH $N_2(X^1\Sigma_g, v=0)$

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The charge transfer reaction

$$Ar^+(^2P_{3/2}) + N_2(X^1\Sigma_g, v=0) \rightarrow Ar(^1S_0) + N_2^+(X^2\Sigma_g, v'') \quad (1)$$

and its inverse

$$N_2^+(X^2\Sigma_g, v'') + Ar(^1S_0) \rightarrow N_2(X^1\Sigma_g, v) + Ar^+(^2P_J) \quad (2)$$

have been extensively investigated by modern techniques capable of probing state-to-state specificity in these reactions. It has been established that reaction (1) gives the v=0 product exclusively at 80° K[1], but that at all temperatures above 140° K the formation of vibrationally-excited levels of the ground electronic state of N_2^+ dominate the reaction kinetics. This has been definitely shown in a laser-induced fluorescence study of the reaction products at a collision energy less than 0.3 eV[2], which indicates that the product ions consist of a distribution of rotational states for the v=0 and v=1 states of the product ion with the vibrationally-excited component constituting 87±10% of the total; the rotational state distribution for N_2^+(v 1) was analyzed in detail, showing $\bar{N}$=12-13 compared with $\bar{N}$≈7 for the N_2 reactant at room temperature. Further, the very strong vibrational state dependence of the reverse reaction (2) has been demonstrated in the elegant study by Govers et al.[3] using electronically and vibrationally state-selected ions.

A recent paper from our laboratory demonstrated the formation of primarily $N_2^+(X^2\Sigma_g, v=1)$ in reaction (1) at collision energies of 1.73 and 4 electron volts.[4] The angular scattering observed in that study showed that the mechanism was direct and that very little momentum was transferred in the electron transfer mechanism. A curve-crossing model was suggested to explain these results. This model has been elaborated in great detail in the work of Govers, et al.[3] who demonstrate that a semi-quantitative rationalization of their results for reaction (2) is possible using the Bauer-Fischer-Gilmore curve-crossing model. That the reaction dynamics of the system is somewhat more complex than deduced from the results referenced above is revealed by the Newton diagram for reaction (1) at a collision energy of 1.1 eV.[5]

The simplest interpretation of the scattering diagram is that vibrational levels 1, 2, and 3 of the product ion are all populated with significant probability and that these products are generated in an angular-specific manner. We have continued our probing of the ArN_2^+ PES by investigating the unreactive scattering of Ar^+. The cross-section for inelastic scattering processes are large and the angular and quantum-state specificity is pronounced.

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20B

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Quantum mechanical microcanonical rate constants from direct calculations of the Green's functions.

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A new method is presented for calculating the quantum mechanical rate constant for a microcanonical ensemble using the flux-flux autocorrelation function. The rate constant is expressed in terms of the coordinate representation of the Green's function which is obtained from the matrix solution of the discretized Schrodinger equation. For one degree of freedom an efficient recursive solution of the discretized equation is presented. The extension of this method to multidimensional systems is discussed.

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20C

INTEGRAL AND DIFFERENTIAL CROSS SECTIONS FOR $Ar^{++}(^3P) + He\ (^1S) \rightarrow Ar^{+}(^2P) + He^{+}(^2S)$ at collision energies from 30 meV to 3 eV

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INTRODUCTION

Most experimental information on low - collision - energy charge tranfer between a doubly charged argon and an helium atom has been obtained using swarm techniques (1). Only recently have state resolved differential cross sections been measured at energies down to 0.5 eV in a crossed beam experiment (2). In order to obtain some more information in the interesting sub- eV range, we have investigated the Ar^{++} + He charge tranfer process in an improved guided beam apparatus. For the first time, not only integral but also absolute values for differential cross sections have been measured with this technique. The probability for the non - adiabatic transition as a function of both, impact parameter and collision energy have been extracted from the results.

EXPERIMENTAL

The guided beam machine is basically the same as the apparatus, previously described (3). Briefly it consists of a storage ion source, RF quadrupole filter (selecting energy and mass), a tandem octopole arrangement with a short scattering cell, a magnetic mass spectrometer and a scintillation detector. Several modifications and improvements extended the accessible laboratory energy range to very low values (with almost constant beam intensity down to 30 meV, lowest energy below 10meV). A long octopole, guiding the ions from the scattering region towards the detector, allows one to determine the axial velocity component of the products via the time of flight (TOF) method. By measuring a set of such TOF distributions for different RF amplitudes (e. g. for different guiding potentials), information on the angular distribution of the products can be extracted in an energy range not accessible to standard crossed beam experiments. The ion source has been operated (low electron energy, high Ar pressure, long storage time) so that the Ar^{++} ion beam consists only of the ^3P ground state.

RESULTS AND DISCUSSION

The dependence of the integral cross section σ (fig 1) from the collision energy E_t can be represented by the formula

$$\sigma = \overline{P(E_t)}\ \pi R_c^2 (1 - V_{POL}(R_c)/E_t)$$

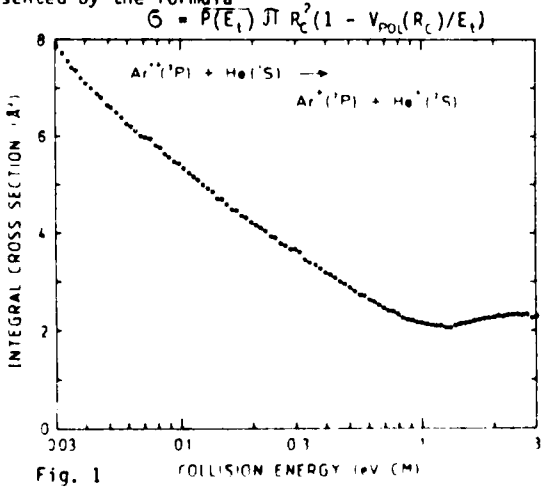

Fig. 1

where R = 4.7 Å is the crossing radius between the polarisation potential $V_{POL}(R)$ and the Coulomb potential, attracting the reactants and repulsing the products, respectively. The (impact parameter averaged) pobability for a charge tranfer, $\overline{P(E_t)}$, has a local minimum of less than .03 at about 1eV. The rise of the cross section towards lower energies is only to a minor part due to the long range attraction. Therefore that change must be explained by the energy dependence of the coupling (Coriolis or radial coupling, or influence of the fine structure).

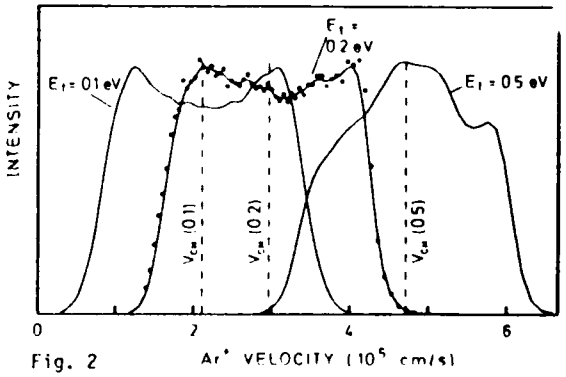

Fig. 2

More detailed information on this coupling can be extracted from the angular distribution of the products. For this simple state to state process (ignoring fine structure), the differential cross section can be determined directly from the axial component of the velocity (guiding all ions independent on their transversal component). Some examples (transformed from the measured TOF distributions) are shown in fig. 2. At low energies, the distributions are symmetric relative to the dashed line (marking the Center of Mass velocity): The differential cross section shows a forward - backward symmetry. Above 0.5 eV, where a pronounced sideways peak is observable, the Ar products are scattered more and more into the forward direction.

This observation is in qualitative aggreement with the results of Friedrich and Herman (2), but there are some discrepancies in the quantitative comparison of the differential cross section at 0.5 eV, in the interpretation of the dominant peak at 90°, and the contribution of the metastable Ar^{++} ions. Experiments with a known mixture of ground and metastable states (using different ion source conditions and analysing the beam by aid of the translational attenuation method (4) are in progress.

ACKNOWLEDGEMENT

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21A

Nonadiabatic Transitions in the Photodissociation of ICN

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Photodissociation of ICN in the A continuum has been modeled assuming all the absorption from the linear ground state is to one diabatic excited state, which dissociates to form I^* ($^2P_{1/2}$) and CN ($^1\Sigma^+$, v=0). This assumption is consistent with previous theoretical considerations and recent experimental observations[1]. It is also assumed that, in nonlinear excited state configurations, nonadiabatic transitions are possible to two distinct surfaces correlating with ground state I ($^2P_{3/2}$) and CN ($^1\Sigma^+$, v=0). Empirical potential surfaces with frozen CN bond lengths are employed, and nonadiabatic transitions between surfaces are treated using both the Tully-Preston surface-hopping model and the Miller-Meyer classical electron picture[3]. Theoretical results obtained with both methods are compared with recent experimental data on the I^*/I branching ratio[4] and product CN rotational distribution[5,6] as a function of photolysis wavelength.

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21B

Laser Spectroscopic and Chemiluminescent Probes of Metal Cluster Structure, Photodissociation, and Oxidation.

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Clusters of the alkali and coinage metals generated through direct supersonic expansion of the pure metal or the metal seeded into an appropriate carrier gas are characterized using laser spectroscopic techniques. The oxidation of these clusters is also considered. The following specific experiments will be outlined:

(1) The development of a cooled Cu_3 (Ag_3) source producing concentrations some six orders of magnitude in excess of those obtained with other methods. We are afforded the opportunity to investigate a far greater portion of the trimer ground and excited state vibronic structure, and are able to probe levels which may be lost to two photon techniques when photodissociation and non-radiative processes are strongly competitive with 'fluorescence'. In addition, there is evidence thet this source will be useful for the study of small particle surface plasmon characteristics.

(2) A study of sodium trimer - halogen atom metatheses using sources used to study alkali trimer photodissociation indicates a rich chemistry including (1) a clear bimodal distribution of Na_2^* product vibrational levels correlating with the dynamics of Na_2 formation, (2) the clear effect of the molecular electronic structure of Na_2 on the dynamics of the reaction $Na_3+X \rightarrow Na_2^*+NaX$, and (3) the observation of stimulated emission from the Na_2 formed in reaction.

(3) The development of a cluster device which lies in the middle ground between a standard effusive source and laser vaporization plasma formation followed by strong supersonic expansion and large widely distributed aggregate formation. High metal fluxes are forced to mild agglomeration in argon or helium at controlled temperatures producing a range of readily adjusted clusters. We will focus on copper and silver oxidation and the formation of metal cluster oxides, ($Cu_xO(2<X<3)$, $Ag_xO(2<x)$.

21C

Time-Resolved Optoacoustic Measurements of the Vibrational Relaxation of Highly Excited Molecules

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Two real-time optoacoustic techniques were used to study the VT relaxation of highly excited polyatomic molecules. In the first method a microphone placed at the wall of a long cylinder measured the interference pattern of the acoustic waves wnich were generated as the excited gas relaxed. In the second method a high frequency piezoelectric ceramic, placed near the center of a large chamber, measured the compression and rarefaction components of a single acoustic wave. Both techniques were used to determine how the rate of vibrational relaxation depends on the amount of energy initially contained in the molecule. Initial measurements were performed with SF_6 in argon, using infrared multiphoton excitation to prepare the vibrational energy distribution of SF_6.

Support by the National Science Foundation and the Petroleum Research Fund is gratfully acknowledged.

22A

Theoretical Study of Intermolecular Energy Transfer Involving Electronically Excited Molecules: $He(^1S) + H_2(B\ ^1\Sigma_u^+)$*

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Improvements in experimental techniques of preparation and detection have increased interest in collision phenomena of electronically excited molecules. In an early experimental study, cross sections for rovibrational energy transfer and electronic quenching were measured for $HD(B\ ^1\Sigma_u^+, v=3, j=2)$, excited by an argon lamp, in the presence of He, Ne, and $HD(X\ ^1\Sigma_g^+)$.[1] In order to better understand these collision processes, the closely related $He + H_2(B\ ^1\Sigma_u^+)$ system is being studied.

An ab initio potential energy surface (pes) has been determined using self-consistent field plus configuration interaction methods. The long-range interactions are described by a multipole expansion. Features of the pes expected to strongly influence energy transfer will be described.

As a first step in the dynamics studies, cross sections for rotational excitation at c.m. energies 0.015-0.165 eV have been computed in the rigid rotator model using the space-fixed coupled-channel formalism and an analytical fit to the ab initio pes. Partial inelastic cross sections display a high degree of structure, which appears to be mainly due to the anisotropy of the interaction energy. The magnitudes of total cross sections for $\Delta j = \pm 2$ transitions are comparable to those for ion-molecule systems.

Progress toward inclusion of rovibrational energy transfer processes will be discussed.

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22B

Application of Synchrotron Radiation to the Study of Molecular Interactions

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A knowledge of the dissociation energies and dissociative ionization pathways of weak polyatomic heterodimers in the gas phase provides important information on long range intermolecular forces and the disposal of vibronic excitation energy. To carry out such studies, molecular beams containing cold heterodimers produced by jet expansion of gas mixtures are ionized by the intense, tunable vacuum ultraviolet photon beams available at the National Synchrotron Light Source at Brookhaven National Laboratory. Product ion mass spectra at given wavelengths and photoionization efficiency spectra at given ion masses are measured using a quadrupole mass spectrometer.

The dissociation energy D(A·B) of the dimer A·B is just the difference between $P_{A,AB}$, the threshold for the dissociative photoionization process $A{\cdot}B + h\nu \rightarrow A^+ + B + e$, and I_A, the ionization energy of A, the partner of lower ionization potential; i.e., $D(A{\cdot}B) = P_{A,AB} - I_A$. To measure $P_{A,AB}$ a subtractive technique is used. The target dimer A·B is formed in a molecular beam by collimation of a jet expansion of mixed A and B gas or vapor, and the wavelength-dependent efficiency for the production of A^+ is measured. A second measurement is made of a molecular beam containing A alone. The second spectrum is normalized to the first at energies just above the ionization energy I_A of A, and the two spectra are subtracted. The result is the desired spectrum for the dissociative photoionization process in its threshold region. A correction is sometimes necessary for the contribution to the first spectrum of A^+ from the dissociative ionization of A·A. In the same experiment, the dissociation energy of the ionic dimer, $D([A{\cdot}B]^+)$, can be determined whenever the ionization potential I_{AB} of the dimer A·B can be measured, via the difference $D([A{\cdot}B]^+) = P_{A,AB} - I_{AB}$. Dissociation energies measured to date are: trans-butene·SO_2, 3.85 ± 0.23 kcal mole^{-1}; $(C_4H_8{\cdot}SO_2)^+$, 2.4 ± 1.2; $(t\text{-}C_4H_8)_2$, 2.9 ± 1.1; 1,3-$C_4H_6{\cdot}SO_2$, 3.24 ± 0.48; $(C_4H_6{\cdot}SO_2)^+$, 3.7 ± 0.9; $C_6H_6{\cdot}SO_2$, 4.40 ± 0.28; $C_6H_6{\cdot}HCl$, 4.79 ± 0.12; $(C_6H_6{\cdot}HCl)^+$, 7.3 ± 1.2.

We find that dissociative ionization pathways that involve fragmentation of one of the partners, viz. $A{\cdot}BC + h\nu \rightarrow AB^+ + C + e$, sometimes occur with probabilities much higher than can be accounted for by RRKM or QET calculations, and that therefore represent nonstatistical processes, few other instances of which are known. Two examples are the processes 1,3-$C_4H_6{\cdot}SO_2 + h\nu \rightarrow (C_4H_6{\cdot}SO)^+ + O + e$ and $C_6H_6HCl \rightarrow C_6H_6Cl^+ + H + e$. The observed onset of $C_6H_6Cl^+$ from $C_6H_6{\cdot}HCl$ at 834 ± 5 Å (14.87 ± 0.09 eV) gives an apparent heat of formation at 0 K of ΔH°_{f0} = 281 ± 2 kcal mole^{-1}. This relatively high value should probably be assigned to an electronically excited state.

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22C

STATE-TO-STATE VIBRATIONAL EXCITATION OF p-DIFLUOROBENZENE IN COLLISIONS WITH HELIUM

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We report the kinetic energy dependence of the total cross sections for the ν = 0- 1, 2 excitation of the ν_{30} mode in p-DFB(S_0) + He collisions. The measurements were made with a variable collision angle, crossed, pulsed molecular beam instrument, utilizing laser induced fluorescence for state selective detection.[1] The kinetic energy range of the measurement includes the vibrational threshold of 20 meV and extends to 325 meV. A search revealed that no other vibrational modes were collisionally excited within the energy range and detection sensitivity of the instrument. The ν_{30} mode is the lowest out-of-plane vibration in p-DFB. Singular excitation in this mode is similar to previous work on aniline,[2] where the two lowest frequency modes were excited, both having out-of-plane geometry.

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23A

Semiclassical and Quantal Investigation of Stretch-Bend Interactions

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For some mode-selective excitation experiments the flow of energy from an excited stretching mode to a bending mode is thought to be the first stage in intramolecular energy flow. We considered a model Hamiltonian consisting of a Morse stretch coupled to a quartic bend. The effect of the nature of this stretch-bend coupling on favorable resonance conditions for energy flow is investigated. Eigenvalues for the Hamiltonians are calculated quantally and semiclassically. The accuracy of various approximate semiclassical methods is studied.

23B

Thermal Rate Constant for $H+CH_3 \rightarrow CH_4$ Recombination. Comparison of Quasiclassical Trajectory and Variationl Transition State Theory

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The variational transition state theory rate constant is calculated for the $H+CH_3 \rightarrow CH_4$ bimolecular reaction and compared with the quasiclassical trajectory value reported previously.[2] The calculations are performed on two different potential energy surfaces, MAPS/CH_4-I and-II. To calculate the variational transition state theory rate constant, the reaction path and frequencies orthogonal to the reaction path are required. The general classical trajectory computer program MERCURY was modified to perform these calculations.

Good agreement is found between the variational transition state theory and quasiclassical trajectory rate constants for both the MAPS/CH_4-I and -II surfaces. The rate constants for the two surfaces differ by an order of magnitude.

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23C

INTERNAL ENERGY RELAXATION IN DIATOMIC MOLECULES MODELED BY EIGENANALYSIS TECHNIQUES

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Internal-energy relaxation is studied by matrix-eigenvalue techniques for two different systems. The first system, a dissociating diatomic dilute in a rare gas, follows a linear master equation, and conventional eigenanalysis is used to examine the competition of internal relaxation with reaction. The second system, vibrational-rotational relaxation including significant effects from diatom-diatom collisions, follows a nonlinear master equation. In this case a linearization procedure is used to allow an eigenanalysis of the relaxation.

In the first study we calculate relaxation times and steady dissociation rates for a shock wave impinging on para-H_2 dilute in Ar. Thermally averaged rate coefficients at 4500K have been computed by Monte Carlo quasiclassical trajectory methods for 659 state-to-state vibrational-rotational transitions. The 162×162 rate matrix is completed by least squares fitting of an analytic form to the calculated rates. Previous investigations on this system[1] assumed rotational equilibrium and found the steady dissociation rate constant to be about 30% less than at local equilibrium as a consequence of the competition of relaxation with reaction. The present study extends these results by including the full rotational-vibrational nonequilibrium effects and gives a steady dissociation rate about a factor of 3 lower than the local-equilibrium value.

The second study is of the relaxation of H_2 in He over the mole fraction range 0-1. The required rate constants were those used by Moise and Pritchard.[2] Previous studies[3] have indicated good agreement of rate constants calculated by numerical integration of a nonlinear master equation with those obtained by eigenanalysis of a linearized one. This study extends the new approach to the case of nonlinear energy relaxation.

This work was supported in part by the National Science Foundation.

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24A

A Theoretical Study of Vibrational Excitation in Diatom-Surface Collisions

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We develop a Gaussian wave packet-mean trajectory[1] technique to study vibrational excitation in diatom-surface collisions. The (anharmonic) vibrational motion of the oscillator is treated quantum mechanically using both coupled and uncoupled Gaussian wave packet techniques.[2-4] The diatom rotates and translates classically under the influence of a potential which is averaged over the vibrational coordinate at each time step, i.e., $V(R,\Theta,\Phi,[X_\lambda]) = \langle \Psi(r) | V(r,R,\Theta,\Phi,[X_\lambda]) | \Psi(r) \rangle_r$, where $\Psi(r)$ is the oscillator wave function expressed as a sum of wave packets, r is the oscillator coordinate, Θ and Φ describe the orientation of the diatom, R is the position of the diatom center of mass, and $[X_\lambda]$ are the positions of the surface atoms. The motion of the surface atoms is incorporated using generalized Langevin techniques.[5,6] Vibrational excitation of heavy diatomic molecules (e.g., Br_2 or I_2) during collisions with fixed and moving surfaces is investigated.

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24B

ABSTRACT FOR SNOWBIRD CONFERENCE

JULY 1985

STATE RESOLVED PHOTOFRAGMENTATION OF OCS MONOMERS AND CLUSTERS

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Recent experiments on OCS photofragmentation dynamics will be presented. In these experiments, OCS in a pulsed supersonic beam was dissociated by a KrCl laser, and either the S atom or CO product was detected by vacuum ultraviolet laser-induced fluorescence. The S atom ^1D:^3P yield was determined to be 85:15, and the CO product was formed in a bimodal rotational distribution, peaking at J' = 56 and J' = 67, reflecting the two S atom channels.

As well, an extremely cold (T_{rot} = 50 K) CO product was observed, and this has been shown to be due to dissociation of OCS in clusters. An S_2 product due to a reaction of the S photoproduct with an OCS in the same cluster was also observed by laser-induced fluorescence.

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24C

Computational Methods for Quantum Mechanical Reactive Scattering

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The quantum mechanical reactive scattering formalism developed by Miller [J. Chem. Phys. 50, 407 (1969)] provides a particularly straightforward method for investigating atom-molecule collision dynamics. Recent applications of this approach within the distorted wave Born approximation--i.e., inelastic (local) interactions treated to infinite order and reactive (exchange) interactions treated to first order--to the standard 1-d and 3-d $H+H_2$ reactions gave quite encouraging results. Extensions to treat the reactive (exchange) interactions also to infinite order have been applied to 1-d $H+H_2$ reaction, with excellent results. However, due to the numerical methods employed in the above calculations, applications of this method in infinite order to 3-d systems remain computationally unfeasible.

Current research efforts focus on approximating the non-local exchange interaction with a separable potential constructed from an L^2 set of functions. Calculations for the 1-d $H+H_2$ reaction, which employ a separable exchange potentaial, are seen to provide reliable reactive scattering probabilities and furthermore reduce the size of the calculation to an acceptable computational level. Future efforts are to apply this method to more interesting chemical applications.

25A

Molecular Beam Studies of the Energy Requirements of Organic Chemiionization Reactions

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We have used two crossed supersonic molecular beams to measure the dependence of the total cross section of several chemiionization reactions, including

$$SbF_5 + RCl \rightarrow SbF_5Cl^- + R^+ \quad (1)$$

$$SbF_5 + TMAE \rightarrow SbF_5^- + TMAE^+ \quad (2)$$

$$SnCl_4 + TMAE \rightarrow SnCl_4^- + TMAE^+ \quad (3)$$

where R = PhCO–, $PhCH_2CO$–, or $(CH_3)_3CCO$–, and TMAE = $(N(CH_3)_2)_2C{=}C(N(CH_3)_2)_2$. For all these reactions, the cross section rises steeply as a function of reactant energy. The measured thresholds are 3.68±0.2 eV for reaction (1) with R=PhCO–, 3.10±0.2 eV for reaction (2), and 3.50±0.2 eV for reaction (3). The result for (3) is in reasonable agreement with the value of 3.2±0.2 eV calculated from previous measurements.[1] For R =$PhCH_2CO$– or $(CH_3)_3CCO$– two organic products are observed: Cl^- transfer, or Cl^- transfer plus loss of CO. By independently varying nozzle temperature and carrier gas, both translational and vibrational energy have been shown to play a significant role in the fragmentation ratio. Earlier work[2] indicates that reaction (1) procedes via long-lived complex, while reactions (2) and (3) are direct. The present results may indicate rapid translational-vibrational energy transfer within the complex.

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25B

THE DYNAMICS OF OH RADICAL DESORPTION FROM Pt SINGLE CRYSTAL SURFACES

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The desorption dynamics of OH radicals formed during the catalytic oxidation of H_2 on clean, well-characterized Pt single crystal surfaces has been investigated. OH radicals were formed by the recombination reaction of co-adsorbed O and H atoms generated on the surface by dissociative chemisorption of both O_2 and H_2. The desorbed OH radicals were detected using laser-induced fluorescence (LIF). Both the OH desorption rate and the OH rotational state distributions were measured as a function of the surface temperature, reactant O/H ratio, surface coverage, and surface structure.

The dependence of the OH desorption yield on surface temperature can be used to deduce an apparent activation energy for desorption of the OH reaction product. The activation energy is found to vary from ~27 kcal/mole to over 50 kcal/mole depending upon the reactant O/H ratio, surface coverage, and surface structure. The implications of these observations in terms of the OH production/desorption dynamics will be discussed.

The rotational state distributions of the desorbed OH radicals are generally found to be Boltzmann and can be characterized by a single rotational temperature which is significantly lower than the surface temperature. For example, as the temperature of a Pt(111) surface was varied over a wide range, the OH rotational temperature was found to be lower than the surface temperature by a constant fraction of ~20% (i.e. T_r/T_s ~0.80). Once the OH radical is formed on the surface it should have a long lifetime prior to desorption during which energy equilibration could take place. The slightly lower rotational temperature observed in comparison to the surface temperature could therefore imply that the desorption mechanism for the chemisorbed OH species involves little or no exit barrier. A comparison of similar data obtained on a polycrystaline Pt surface, a highly stepped Pt(111) surface, and a Pt(100) surface will also be presented.

*Work performed during tenure as a NRC/NRL Postdoctoral Research Associate. Present address: Chemical Kinetics Division, National Bureau of Standards, Gaithersburg, MD 20899.

25C

A Trajectorized Quantum Model for Surface Harpooning Processes Occurring in Diatom-Surface Scattering.

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The dynamics of diatomic molecule-surface collisions involving charge transfer between the partners is presented within a framework in which the center-of-mass translational motion is treated classically with a trajectory approximation (TA) and the intramolecular vibrational motion quantum mechanically at various levels of sophistication. State-to-state T→V probabilities, mean energy transfer to the vibrational system, and dissociation probabilities are calculated for parameters which model N_2 and halogen molecules and the results are considered within the context of both the "exact" classical mechanics results presented in our companion paper, and also experimental results due to Kolodney and coworkers.

The role of molecular orientation on the charge transfer/surface hopping probability is considered in the light of the electronic band structure of the physical surface and some molecular beam experiments involving internal vibrational excitation are proposed which take advantage of the orientational dependence of the Landau-Zener probability.

26A

LASER INITIATED HALF-REACTION: NO FORMATION FROM N_2O DIMER VIA $N_2O \cdot O(^1D)$ REACTANT PAIR

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Laser initiated half-reaction, $(N_2O)_2$ + 193 nm -> $N_2O \cdot O(^1D)$+ N_2 -> 2NO + N_2, has been observed by using a molecular beam mass spectrometer. Nitrous oxide dimer beam was generated by a supersonic expansion through a nozzle-skimmer system. When 193 nm radiation of ArF laser was focused onto the beam, NO^+ was detected. The intensity of NO^+ signal was proportional to the $(N_2O)_2$ concentration. The observed laser power dependence of NO^+ ion intensity suggests the following three-step mechanism starting from $(N_2O)_2$; the photodissociation of one monomer N_2O, followed by the intra-molecular reaction producing NO, and the two-photon ionization of product NO to form NO^+.

26B

GENERAL FEATURES FOR THE REACTION DYNAMICS OF CHARGE-TRANSFER REACTIONS AS REVEALED BY THE CROSSED-MOLECULAR BEAM METHOD

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Over the past three years we have investigated the molecular dynamics of a number of simple atomic and diatomic ions/atomic and diatomic neutral charge-transfer reactions. These experiments have provided evidence for three general mechanisms: (1) A mechanism which can be described as an "electron jump" which involves very little exchange of energy or angular momentum between the colliding partners; (2) a "collision-complex" mechanism in which the scattering of the reactive partners is symmetric about the center of mass velocity vector and in which extensive exchange of energy and angular momentum between the collision partners is observed; and (3) a mechanism in which specific quantum states are formed as the dominant reaction channel. These latter reactions may be classified for discussion purposes as following a "curve-crossing" mechanism.

Although only a few systems have been studied thus far in sufficient detail to define these reaction mechanisms, some of the key characteristics which determine whether a reaction pair is likely to follow one or the other of the reaction models described above are reasonably well-established. The complex model requires, for example, that the reaction partners sample a potential surface with a potential well depth which is comparable to the collision energy at which the experiment is carried out; these reactions require binding forces much larger than those which can be accounted for by invoking ion/induced dipole, ion/dipole or ion/quadrupole forces. Direct mechanisms (1) and/or (3) are followed whenever this feature is absent. Examples of the three types of reaction mechanisms will be presented and discussed.

26C

ISOMERIZATION DYNAMICS VIA MODE-MODE ENERGY TRANSFER

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A number of recent experiments have examined isomerization and decomposition of molecules following direct laser excitation of overtones of local vibrations. These studies generally find that reaction rates are well-described by statistical theory, thus indicating a lack of mode-specific chemistry. To assist in understanding these results, we have studied the classical dynamics of intramolecular mode-mode energy transfer in molecules excited above isomerization thresholds. In the first study, we have determined the probability of isomerization of hydrogen isocyanide (HNC → HCN) following excitation of the HN vibration to various v states. It was found that the probability does <u>not</u> increase monotonically with energy. This non-statistical result is due to a highly specific transfer of energy from the HN stretch to a <u>combination</u> of the CN stretch and the H-wagging reaction coordinate, due to a combination nonlinear resonance.

In the second study, we have analyzed the vibrational dynamics of the 1,5 hydrogen shift in β-hydroxy acrolein (Malonaldehyde). We have found that a quasi-periodic resonant exchange of energy between the O-H stretch and the C-O-H bend is critical to the hydrogen shift isomerization. We have calculated reaction times analytically from the stretch-bend phase relations, and have also determined the conditions under which isomerization is <u>classically forbidden</u> at energies above the reaction barrier.

27A

QUANTIZED SEMICLASSICAL TRAJECTORY APPROACH FOR EVALUATION OF VIBRONIC TRANSITIONS IN ANHARMONIC MOLECULES[1]

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ABSTRACT

Significant progress has been made in recent years in simulation of molecular spectra. It appears, however, that the available methods do not offer a reliable and practical way for simulation of the vibronic line shapes of large anharmonic molecules. As a step in the effort of attacking this problem we develop a semiclassical approach that generates quantized vibronic transitions between electronic surfaces of anharmonic molecules. The method evaluates vibronic transition probabilities by using the energy representation (Green's functions) of the corresponding semiclassical propagators. The resulting expression generates automatically interference effects for nonquantized actions and gives significant intensity only for quantized vibronic transitions. This method is compared to other semiclassical approaches and shown to produce much better result for highly anharmonic system. The problem with other approaches (including the Gaussian wavepacket methods) is shown to be related to the fact that they do not contain information from trajectories at the relevant energies.

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27B

THE INCLUSION OF VIBRATIONAL ANHARMONICITY IN THE CALCULATION OF ACCURATE RATE CONSTANTS FOR POLYATOMIC REACTIONS

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The first-principles calculation of accurate thermal rate constants for elementary reactions has been a subject of major importance for many years, not only as an alternative to experiment, but also as an aid to understanding what factors control reaction rates. Canonical variational transition state theory (CVT) has proved to be a practical approach for polyatomic systems for a given potential energy surface. In CVT the rate constant is obtained by approximating the flux of reactive trajectories across a hypersurface that divides reactants from products, and variationally optimizing the location of this dividing surface. A major component of this method involves calculating the quantal partition function for the vibrational degrees of freedom orthogonal to the dividing surface, which are bound by an anharmonic potential energy surface. Inclusion of the polyatomic anharmonic vibrational contributions is thus important for obtaining accurate results. In the current implementation of CVT for polyatomic systems, only the anharmonicity within individual normal modes of the transition state has been included, while the coupling terms between the modes have been neglected. However, the neglect of the mode-mode couplings can lead to serious errors in the partition functions[1]. To incorporate such contributions in a practical manner, we model the vibrational potential in each internal coordinate (i.e., stretch and bend) by a simple functional form (e.g., a Morse potential). Following a transformation of the force constants to normal coordinates, the quantal partition function can be approximated from the zero-point energy (which can be obtained from perturbation theory) and the corresponding classical partition function for the effective potential energy surface [2]. In this talk, we first compare the results for the vibrational partition functions of some triatomic molecules obtained with various choices for the functional form of the vibrational potential in each type of internal coordinate to the accurate results for these molecules. We then discuss the application of this approach to the calculation of the anharmonic rate constant for the reaction $OH + H \rightarrow H_2O + H$.

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27C

Rotationally Inelastic Molecular Beam Diffraction from Finite Temperature Surfaces

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We present new time dependent methods for the study of rotationally inelastic gas-surface diffraction. The translation of the molecule is described using Gaussian wave packet trajectories.[1,2] The methods make no sudden or decoupling approximations, treating the surface corrugation in a non-perturbative manner, thus giving information on transitions which don't conserve m_J. In one limit, a single packet at a time is propagated, using a rotationally averaged potential. This mean trajectory case compares very well with two recent perturbative close coupling calculations.[3,4] A more exact multiple trajectory technique is also presented. In addition, the method provides a very intuitive physical picture, showing how rotational transitions effect the beam coherence, modulating diffraction peak amplitudes.

As done previously for He diffraction,[5] the effects of finite temperature are incorporated by allowing the surface atoms to move classically, using generalized Langevin techniques.[6,7] This allows for both energy transfer and Debye-Waller attenuation.

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28A

The Quantization of Symmetric and Weakly Nonintegrable Hamiltonian Systems

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The construction of a classical analog for symmetric and weakly nonintegrable Hamiltonian systems is outlined by the means of three examples. The method of construction is based upon the density matrix formulation of classical and quantum mechanics. The energy levels of the classical analog of the Henon-Heiles Hamiltonian system are compared with the quantum and semiclassical results.

QUANTUM MECHANICAL RATE CONSTANTS VIA PATH INTEGRALS: DIFFUSION OF HYDROGEN ATOMS ON A W(100) SURFACE

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Using Monte Carlo path integral methods described recently by Miller et al. /1/, quantum mechanical rate constants have been calculated for diffusion of H atoms on a model W(100) surface /2/. The most interesting aspect of the present work is that it includes the effect of surface atom motion, i.e. phonons, on the H atom tunneling dynamics. Although the description is fully quantum mechanical, the phonons enter the present path integral treatment in a way very similar to how they appear in the classical generalized Langevin models; the present formulation thus provides the correct quantum mechanical analog to classical frictional effects. The principal qualitative result shown by the calculations is that surface atom motion increases the rate of H atom tunneling from one stable site on the surface to another.

Having investigated the simple process of diffusion of single hydrogen atom, we are now interested in describing chemical reactions on surfaces, for example the recombination and desorption of hydrogen,

$$\text{surface} \begin{matrix} \nearrow \text{H} \\ \searrow \text{H} \end{matrix} \longrightarrow \text{surface} + H_2$$

and, in particular, wish to study the effects of surface atom motion. These investigations are now in progress.

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Z 8C

CHEMICAL DYNAMICS STUDIED BY POSITRONIUM AND MUONIUM ATOMS

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Positronium (Ps) and Muonium (Mu) atoms have been employed as the lightest and very light atoms to investigate chemical kinetics in solutions. Due to their light masses, the classical transition-state-theory (TST) can not fully interpret the observed rate constant variations with temperature. The observed rate constants reach a maximum at certain temperature but decrease at either higher or lower temperatures. A new interpretation based on Kramers theory (1940) in terms of solvent effect is presented.

29A

Semiclassical Quantization via the Adiabatic Hypothesis

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In this work we analyze and further develop the adiabatic invariance method for computing semiclassical eigenvalues and propose a new use to calculate final state action variables in scattering problems. This method, which was recently introduced by Solov'ev, is basically an application of the Ehrenfest adiabatic hypothesis which states that a system in a quantum allowable state will remain in that state as the system is externally and adiabatically altered and further, that the dynamical behavior during this change can be described by conventional mechanics. The eigenvalues are determined from a classical calculation of the energy as the time dependent Hamiltonian $H(t) = H_0 + s(t)H_1$ is switched adiabatically from the separable reference Hamiltonian H_0 to the system Hamiltonian $H_0 + H_1$. A systematic study is carried out to determine the best form for the switching function, $s(t)$, to maximize the rate of convergence of the energy to its adiabatic limit. Five switching functions, including the linear function used by Solov'ev, are defined and tested on three different systems. The linear function is found to have a very slow convergence rate compared to the others. The classical energy is shown to be a periodic function of the angle coordinates of H_0. The coefficients of the Fourier series representation of this function are then shown to be related to the classical energy expectation value and classical energy uncertainty which we define and compare to their quantum mechanical counterparts. Four example problems are analyzed and solved in the course of this investigation. They are; (i) the forced harmonic oscillator, (ii) the harmonic oscillator with time dependent frequency, (iii) the nondegenerate and (iv) the degenerate two dimensional coupled oscillator problems. In the degenerate oscillator case, we have discovered a correction, similar to the Langer correction in WKB theory, which significantly increases the accuracy of the semiclassical eigenvalues. Mixed states, i.e. states that are a linear combination of several energy eigenstates are discussed and it is demonstrated that the energy expectation value of these mixed states can be computed semiclassically.

29B

SPECTRA AND DYNAMICS OF INFRARED PHOTODISSOCIATION OF VAN DER WAALS DIMERS

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The spectra and product velocity distribution have been measured for the photodissociation of several van der Waals and hydrogen-bonded dimers. Specifically, measurements of ethylene-hydrogen chloride, benzene dimers, and silane dimers. These measurements are part of various studies of intramolecular energy transfer.

The energy initially placed into a dimer by exciting a vibration can migrate to and rupture the weak van der Waals bond. A spectra consists of measuring the fraction dissociated as a function of the laser wavelength. The width of this curve is related to the lifetime of the state initially excited. By measuring the velocity distribution of the products and knowing how much energy was placed in the dimer by the absorbed photon, and knowing the weak bond strength, one can obtain how much energy is left to the internal modes of the monomer products. These two measurements help elucidate energy transfer mechanisms.

29C

POLARIZATION DEPENDENCE OF ASSOCIATIVE IONIZATION AND OF LASER-INDUCED CHEMI-IONIZATION AND EXCITATION TRANSFER

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We present a theory to aid in the interpretation of experimental studies of inelastic collisions involving laser-prepared atoms and/or laser-induced electronic transitions. For associative ionization, laser-induced chemi-ionization and excitation transfer, one can derive equations for the total cross section as functions of polarization. Specifically, the total cross section σ_T depends on 1) (generally unknown) state- and reaction - specific cross sections σ_i and 2) explicit functions of the angle γ between the laser polarization axis and the direction of initial atomic momentum. The number of σ_i which are non-zero is limited by selection rules. Then, comparison of our theoretical relations with experiment allows one to place constraints on relative values of the σ_i. Thus, one can obtain information both about the relative rates of competing processes and about the identity of reactive electronic states.

We[1] have recently applied this procedure to the thermal beam experiments of Kircz, Morgenstern and Nienhuis[2], who measured $\sigma_T(\gamma)$ for the reaction

$$(1)\quad 2Na[(3p)\,^2P_{3/2}] \rightarrow X\,^2\Sigma_g^+\ Na_2^+ + e^-.$$

It is found that at least two quasimolecular states of Na_2 participate in (1), that is, at least two σ_i must be non-zero to obtain reasonable agreement with experiment. Further, it is found that the dominant contribution arises from the $1\Sigma_g^+$ state with asymptotic configuration σ_g^2-σ_u^2. Our results can also be applied to other processes, for example the two color experiment[3]

$$(2)\quad 2Na(3s) \xrightarrow[\hbar\omega]{(D_2)} Na(3s) + Na(3p) \rightarrow [Na...Na] \xrightarrow[\hbar\omega']{} [Na...Na]^+ + e^-$$

$$\rightarrow \begin{cases} Na_2^+ + e^- \\ Na + Na^+ + e^-. \end{cases}$$

Here, differences between the intensity and polarization dependences of (2) and competing ionization processes (e.g. photoionization of neutral dimers) are identifying characteristics which can be used to extract cross section information about individual reactions.

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30A

PHOTODISSOCIATION DYNAMICS OF ICN

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An understanding of the detailed dynamics of the photofragmentation process is important in the elucidation of many photochemical systems. Because of the nature of the bound-free transition, the absorption spectra of many single-photon dissociation processes are broad and featureless. In order to learn about the excited state(s) and dissociative potential energy surface(s) involved in the photofragmentation processes, it is therefore necessary to examine in detail the final state distribution of photofragments.

We have been studying the photodissociation of ICN. The goal is to try and learn as much as possible about the dynamics of the photodissociation process by examining the final state distribution of the CN fragment in as much detail as possible. ICN, at pressures of 10-20 mTorr, is dissociated by 249 nm radiation from an excimer laser. The excimer laser is also used to pump a tunable dye laser which probes the CN $X^2\Sigma^+$ distribution after a delay on the order of 20 nsec. The CN fragments are produced in their ground electronic state, and the dye laser is tuned through the CN $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ transition to probe the final state distribution via laser induced fluorescence (LIF).

In addition to conventional measurements of vibrational and rotational populations, we are studying the alignment of angular momentum in the CN fragment. This can be determined by observing the variation in fluorescence intensity as the probe laser's polarization is rotated with respect to the direction of polarization of the photolysis laser. When such a measurement is made for a single N" level in the final CN $X^2\Sigma^+$ distribution, the second multipole moment of the M_N" distribution is exactly determined.[1]

Another vector quantity that we can measure is the angular distribution of photofragments. For a linearly polarized photolysis, the normalized angular distribution of photofragments is given by

$$f(\theta) = \frac{1}{4\pi}\{1 + \beta P_2(\cos\theta)\}$$

where $P_2(x) = \frac{1}{2}(3x^2 - 1)$.[2] In this system, the atomic iodine fragment has no internal degrees of freedom, and the CN fragment's velocity is fixed once its internal energy is known. The [illegible] of the [illegible] transition will [illegible] of the CN fragment relative to the [illegible] polarization.[1]

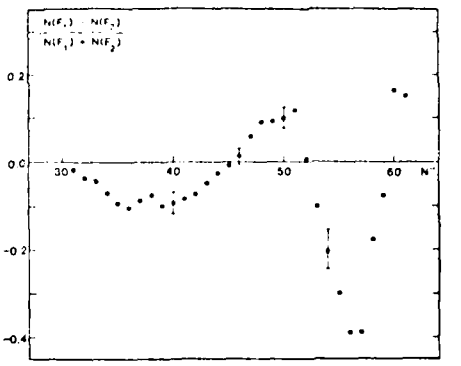

Figure 1 Population differences of the F_1 and F_2 spin-rotation doublets over total population as a function of rotational quantum number N" for CN $X^2\Sigma^+(v''=2)$ produced in the photodissociation of ICN at 249 nm.

In the course of this study, we have also observed that the two spin-rotation components (F_1 and F_2) of the CN $X^2\Sigma^+$ fragment are unequally populated and that this difference in population changes as a function of N". This has previously been observed by Wittig and co-workers in the dissociation of ICN and BrCN at 266 nm.[4] In Figure 1, the difference in population of the spin-rotation doublets divided by the total population of the two levels is plotted as a function of rotational quantum number N". The population differences clearly oscillate and tend to increase with N". This effect is attributed to interactions between the spins and angular momenta of the iodine and CN fragments. The interactions and couplings between the various angular momenta will be mediated by the dissociative potential energy surface, and so these population differences are expected to be a very sensitive function of the dynamics of the photodissociation process.

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UNIMOLECULAR AND COLLISION INDUCED FRAGMENTATION [illegible]

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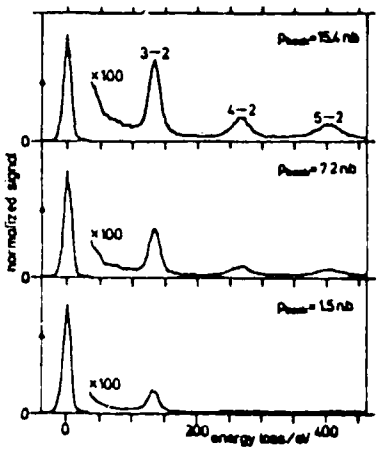
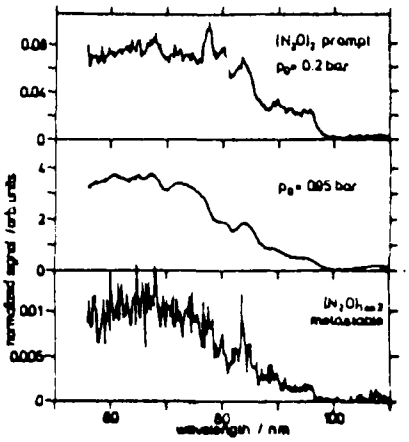
$(N_2O)_n$-clusters, n=1...5, formed in a supersonic jet [illegible] from the electron storage ring BESSY at Berlin (wavelength [illegible] λ [illegible]) were accelerated, passed a field free drift region and were [illegible] quadrupole mass filter and a 90° electrostatic deflector. [illegible] mentation process $m^+ \rightarrow m^+_0 + \Delta m$ somewhere on their way [illegible] energy $e \cdot U(t)$ they will lose a fraction $\Delta m/m$ of that energy [illegible] [1] [illegible] fragmentation processes occuring within the field free [illegible] ..6.3)µs) give rise to a peak in the observed ion current [illegible] scanned. Fig.1 shows energy loss scans at three different [illegible] show, that only the removal of a single neutral N_2O from the [illegible] decay. The removal of more than 1 molecule is collision [illegible]

Photoionization efficiency (PIE-) curves were measured [illegible] citation region and for the metastable ions dissociating [illegible] threshold shape changes significantly with clustersize, [illegible] lar indicating similar binding energies. Surprisingly [illegible] and the basically rectangular shape of the thermal [illegible] ions are formed initially with a rather well defined [illegible] dent photon energy. Any excess energy breaks the weak [illegible] whereas our prompt dimer spectrum at p_0 [illegible] bar [illegible] the spectrum shows more pronounced structure [illegible] of clusters with n≥3 in the jet is reduced [illegible] tion similar to the monomer [illegible] in contrast to the prompt channel.

More experimental results will be presented at [illegible] supported by the Bundesministerium für [illegible]



[illegible] energy loss scans for N_2O^+ at three [illegible] different background pressures $n \rightarrow (n-m)$ [illegible] $(N_2O)_n^+ \rightarrow (N_2O)^+_{n-m} + (N_2O)_m$



[illegible]

[1] [illegible]
[2] [illegible]
[3] [illegible]

[illegible] Summary

[illegible] Berlin [illegible] and energy se- [illegible] may undergo a [illegible] by [illegible] will [illegible] which frag- [illegible] by [illegible] [1]).

[illegible] (Fig. 1c) are [illegible] is below ~0.5 bar [illegible] around 194 nm and [illegible] the PIE-spectrum [illegible] heterogene- [illegible] and a benzonitrile- [illegible] (Fig. 1a) and well above [illegible] ionization lines in the [illegible] - to a large extend - to [illegible] at ~[illegible] for Kr at ~90nm) occurs close [illegible] be attributed to excitation of Ar (Kr) [illegible] of the cluster.

[illegible] M_u^+ [illegible] by "spontaneous" (>0.4μs) and by [illegible] $C_6H_5CN^+$ showing that the major increase in [illegible] shifts considerably towards lower [illegible] metastable [illegible] is selected. Other measurements show that the total frag- [illegible] as well as the shape of the PIE- [illegible] curves changes significantly if higher stagna- [illegible] 2 bar) are used. Whether these effects are due to cluster formations only or [illegible] of the beam is presently under investigation. The dependence of the me- [illegible] background pressure is studied and also the extraction voltage is varied [illegible] the $C_6H_5CN^+$-lifetimes for distinct fragmentation channels. All these meas- [illegible] will be presented and discussed at the conference. This work was supported by the [illegible] Ministerium für Forschung und Technologie.

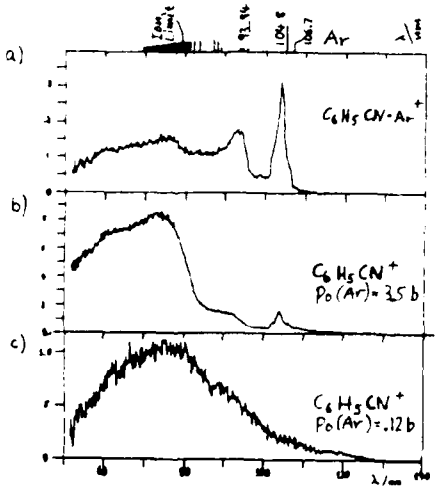
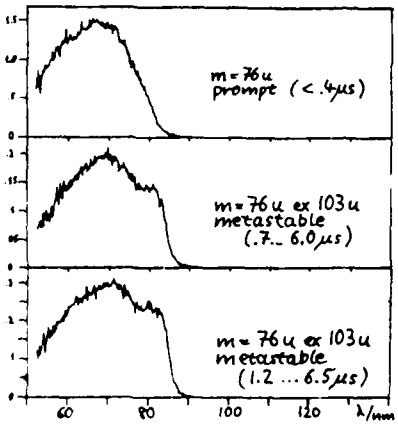


Fig. 1 Prompt PIE-spectra [illegible]
b) [illegible] C_6H_5CN seeded with [illegible]
c) [illegible] C_6H_5CN [illegible]



[illegible] for $C_6H_4^+$ being [illegible] spontaneous and [illegible] of $C_6H_5CN^+$

References:

[1] [illegible]

31A

ABSTRACT SUBMITTED FOR THE

CONFERENCE ON THE DYNAMICS

OF MOLECULAR COLLISIONS

SNOWBIRD, UTAH, JULY 14-19, 1985

A Classical Trajectory Surface Hopping approach to Non-adiabatic Processes occurring during diatom-surface scattering.

M. KARIKORPI and S. HOLLOWAY, University of Liverpool.

J. W. GADZUK, NBS.

The dynamics of diatomic molecule - surface collisions involving charge transfer processes between the partners is presented. The motion of the molecule over model diabatic potential energy surfaces is considered assuming that charge harpooning can take place along the seam where the potential energies of the relevant electronic states are equal. The probability for hopping onto a new potential energy surface or remaining on the initial one is determined in the Landau-Zener-Tully-Preston picture paying special attention to the significance that the molecular affinity level position and width have on the branching ratios. We report here on a study of the energy redistribution among the intramolecular and translational degrees of freedom arising from the formation of temporary molecular ions and evaluate the probabilities of incoming molecules being either dissociatively adsorbed or scattered as neutrals or molecular ions. The special properties of the potentials responsible for quasi-periodic vs. chaotic behaviour are studied focusing on the role which the nature of the dynamics has on both the evolution of the process and the derived branching ratios.

31B

GENERATION AND RELAXATION OF VIBRATIONALLY-EXCITED H_2 MOLECULES BY WALL COLLISIONS.

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Abstract

Computer molecular dynamics has been used to study the de-excitation as well as the production, of vibrationally-exicted H_2 molecules during both single and repeated wall collisions. Initial vibrational states range from v" = 2 to v" = 12 and the initial translational energies range from thermal (i.e., around 500 K) to 100 eV. The average loss or gain of vibrational, rotational, translational, and total molecular energies for a statistically-significant number of molecules has been evaluated. At the higher translational energies (1 - 100 eV) a substantial fraction of the molecules survive with large (v" > 6) vibrational energy. At lower, thermal, energies vibrational de-excitation predominates; the loss of total molecular energy to the wall (accommodation) is in the three to four percent range, whereas energy redistribution leading to equipartition among the molecular degrees of freedom occurs rapidly and is essentially achieved after three to four collisions with the surface. A computer-generated film will illustrate some of the salient points of the presentation.

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*Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

1282N.3/25/85

31C

AN MPI STUDY OF ROTATIONAL RELAXATION IN PULSED NH_3 EXPANSIONS

by

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ABSTRACT

We have employed resonant enhanced multiphoton ionization (MPI) spectroscopy to probe the rotational relaxation of NH_3 in pulsed supersonic expansions. These quantum resolved measurements have been performed under numerous stagnation conditions employing both neat and seeded NH_3 beams. Our results indicate that different nuclear spin modifications (ortho-para) of NH_3 rotationally relax at different rates; such findings are explained on the basis of rotational state density and energy-gap considerations. Direct spectroscopic evidence for energy partitioning of clustering enthalpy into monomer rotation is observed under stagnation conditions which favor cluster formation. The mechanism for such energy transfer is based on competition between monomer rotational relaxation and cluster formation. The details of the experimental observations and their implications will be discussed.

*This work performed at Sandia National Laboratories supported by the U. S. Department of Energy under contract number DE-AC04-76DP00789.

32 A

Empirical Potential for the He + CO_2 Interaction: Multi-Property Fitting in the Infinite-Order Sudden Approximation. M. KEIL and G.A. PARKER, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

An empirical intermolecular potential for the interaction of He with CO_2 is obtained via data reduction of phenomenological cross sections. The infinite order approximation is used to calculate the total differential, total integrated, and spectral line broadening cross sections, and diffusion, viscosity, thermal conductivity, thermal diffusion factors and second virial coefficients. Second order Chapman-Cowling corrections were used to determine some of the transport coefficients and quantum corrections to the classical virial coefficients were included. The empirical potential obtained simultaneously fits all nine different types of experimental data to within their experimental error and the computational accuracy.

32B

Laser Absorption Profiles of a Reactive Collision Complex: $Mg + H_2$

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We report on preliminary experimental studies of the far wing absorption of laser light into the MgH_2 reactive collision complex. We have measured the far wing absorption profile leading to both the non-reactive channel (Mg* formation) and into specific vibrational-rotational levels of the reactive channel (MgH (v" = 0, J" = 23) and MgH (v" = 0, J" = 6) formation).

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Abstract Submitted for the 1985 Conference on the Dynamics of Molecular Colls.

32C

Transfered Angular Momentum Projections in Reactive Scattering; $H + D_2 \rightarrow HD + D$, $H + H_2 \rightarrow H_2 + H$. C.R. KLEIN, C.K. LUTRUS, and S.H. SUCK SALK, Univ. of Missouri-Rolla -- Previously it was found that rovibrational state-to-state reactive transitions are dominated by the largest angular momentum transfer for the case of collinearly favored reactions[1]. Here we examine the importance of projection quantum numbers in studying reaction mechanisms. From the knowledge of favored transfered angular momentum and its projections we find that the dominant configuration of the triatomic system during collision is well understood. For the reactions studyed it is found that cross sections exhibit dominance of the largest transfered angular momentum and of the projection quantum number of the transfered angular momentum m=0.

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33A

ELEMENTARY CATASTROPHES IN SURFACE SCATTERING

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Rainbow scattering of atoms or ions from solid surfaces is a well known phenomenon. It gives information about the collision dynamics and hence about the interaction potential between projectile and solid. The rainbows appear in plots of the scattered intensity versus the s attering angle. More complex rainbows can be seen when the scattered intensity is plotted as a function of both the scattering angle and the energy transfer to the solid (1). The latter experiments have been performed for the system K + W(110) at energies around 40 eV and normal incidence. The data indicated that there is a strong azimuthal dependence of the intensity, leading to so-called "real" rainbows of the triple differential cross section, a root of the corresponding 3 by 3 determinant.

In the experiments performed so far the azimuthal dependence is not studied directly, i.e. only data taken at various azimuthal angles is compared. In the present study the azimuthal dependence is studied directly and the data is presented in polar plots. In these plots cusplike features are present. These features are indicative of so-called elementary catastrophes, in this case of the hyperbolic umbillic type.

Elementary catastrophes are a mathematical way to catagorize singularities arizing from the mapping of continuous functions on others. Rainbows are an example of a catastrophe in only one degree of freedom. More complex "rainbows" are in fact examples of catastrophes. The importance of elementary catastrophes in light scattering and surface scattering has been demonstrated by Berry (2). In his calculations, however, model systems have been used which are not applicable directly to a real surface scattering situation.

We will demonstrate that elementary catastrophes can be observed on experimental results for the scattering of K atoms from W(110) in the cusp-like structures already mentioned. The experiments can be reproduced using classical trajectory calculations with a realistic interaction potential. In addition, model calculations will be presented using more simple expressions for the potential, like sinewave corrugation of a hard wall or overlapping hard spheres. From the comparison of these calculations with experiment it is clear that the elementary catastrophes observed reflect the symmetry of the interaction potential at the surface and thus can serve as a very powerful tool in the study of the dynamics of the gas-surface interaction.

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33B

Vibrational-State Selected Ion-Molecule Reactions in the $O_2^+(X^2\Pi_g) + CH_4$ System

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Using the TESICO technique[1], vibrational-state selected reaction cross sections have been determined for the three channels of the reaction of O_2^+ with CH_4, viz.,

$$O_2^+ + CH_4 \rightarrow CH_3O_2^+ + H + 4.70\ \text{eV} \quad (1)$$

$$\rightarrow CH_3^+ + HO_2 - 0.26\ \text{eV} \quad (2)$$

$$\rightarrow CH_4^+ + O_2 - 0.48\ \text{eV}. \quad (3)$$

The vibrational states selected are v = 0 - 3 of the $O_2^+(X^2\Pi_g)$ ion with vibratioal quantum of about 0.23 eV.

At a collision energy of 0.27 eV, the cross section for exoergic channel (1) has been found to increase sharply as vibrational quantum number v increases from 0 to 2 but decrease sharply in going from v = 2 to v = 3. Endoergic channels (2) and (3), which have negligibly small cross sections when v = 0, become significant at v = 1 and are further enhanced at v = 2, but their cross sections are still much smaller than that of channel (1). In going from v = 2 to v = 3, however, the increase in the cross section of channel (3) is dramatic and the CH_4^+ ion becomes by far the most abundant product ion. The cross section of channel (2) is also enhanced considerably at v = 3, having a value comparable to that of channel (1).

When overall cross section is plotted versus total energy (i.e., $E_{trans} + E_{vib}$), our results are found to agree very well with those of flow-drift tube study with He buffer gas[2], where all reactant ions are believed to be in the ground state and thus the total energy represents collision energy.

1) I. Koyano and K. Tanaka, J. Chem. Phys. 72, 4858 (1980)
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33C

N-Particle Scattering Equations and Surface Functions in Hyperspherical Coordinates

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An explicit expression for the hamiltonian operator for a system of N particles in hyperspherical coordinates will be given. The body-fixed surface function and scattering equations, after removal of the overall system rotation, will be presented, as well as the resulting coupled channel equations. An application of this formalism to 4 particle systems will be given.

34A

Molecular Dynamics of Non-Equilibrium Infrequent Events: Laser Induced Desorption from Surfaces

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ABSTRACT

An obvious shortening of classical trajectory simulations of chemical reactions is their limitation to short timescale processes. While procedures to extend simulations to long timescales have been developed for equilibrium reaction systems, there are no techniques for nonequilibrium situations. We propose such a method, which employs information theory analysis of short-time trajectory results, and apply it to selective laser-induced desorption of molecules from surfaces.

We illustrate the method by simulating laser-induced desorption of Xe from Pt(111). Desorption rate constants obtained under equilibrium conditions agree with those calculated by standard equilibrium infrequent event methods. They also agree with the values obtained from direct simulation in the high temperature (fast timescale) limit. We have examined the dependence of laser-induced desorption on the laser frequency and field strength and the surface temperature. Enhanced desorption is observed at surprisingly low temperatures and field strengths. The final surface temperatures which are similar to the initial ones, indicate non-thermal selective desorption and the velocity distributions of desorbed Xe atoms are highly non-Boltzmann. Applications to the laser-induced desorption of NO from LiF will be discussed.

34B

Dependence of the collision-induced ro-vibrational excitation on the rotational-state density.

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To effect a rigorous study of the above title, the close coupling scheme of Eastes and Secrest, the Gordon-Secrest He-H_2 potential, and the basis set {10,8,6} are used. The total energy of the colliding system is set at 0.941 eV, or 3.5 times the zero point energy of the hydrogen molecule.
Calculations were done for three systems: He-H_2 and two involving imaginary diatomic molecules, H_2' and H_2''. Vibrational motions of all three molecules are described by an identical harmonic oscillator while their rotational states are adjusted by varying y_0 in the internal energy expression $E_{vj} = 2_v + 1 + j(j+1)/(y_0^2+v+0.5)$ such that

$E_{0,10}(H_2'') = E_{0,6}(H_2)$; $\qquad 2E_{0,10}(H_2') = E_{0,6}(H_2) + E_{0,8}(H_2)$.

This gives rise to four, five, and six <u>effective</u> rotational states in each vibrational manifold of H_2, H_2', and H_2'', respectively.

The results are summarized in a table.

	H_2	H_2'	H_2''
$\sigma_{(0,0)\to 0}$	4.129 +0	4.793 +0	4.921 +0
$\sigma_{(0,0)\to 1}$	6.146 -8	4.395 -8	4.101 -8
$\sigma_{(0,0)}$	4.439 +1	4.437 +1	4.431 +1

$\sigma_{(0,0)\to 0} = \sum_{j\neq 0} \sigma_{(0,0)\to(0,j)}$; $\qquad \sigma_{(0,0)\to 1} = \sum_j \sigma_{(0,0)\to(1,j)}$;

$\sigma_{(0,0)} = \sum_{v,j} \sigma_{(0,0)\to(v,j)}$.

These values clearly indicate that

1. the rotational-state density has no effect on the total cross sections $\sigma_{(0,0)}$;
2. while a higher state density promotes the total excitation from the state (0,0), $\sigma_{(0,0)\to 0} + \sigma_{(0,0)\to 1}$;
3. it, in fact, reduces the vibrational excitation cross sections, $\sigma_{(0,0)\to 1}$.

34C

Nascent Rotational Product State Distribution in the Charge Transfer Reaction of $N^+ + CO \rightarrow CO^+ + N$ at Near Thermal Energy

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An improved ion beam apparatus is used to measure the nascent rotational state distributions in the charge transfer reaction $N^+ + CO \rightarrow CO^+ + N$ for both the major and minor vibrational channels under single-collision conditions. In the major vibrational channel, v = 0, the rotational distribution under single collision conditions can be characterized by a Boltzmann distribution with the temperaure T = 430 ± 30 K. The rotational temperature decreases to room temperature when secondary collisions cause relaxation at higher CO densities. In the minor vibrational channel, v = 1, the primary results show that the rotational distribution is highly excited and non-Boltzmann. For high rotational quantum number ($K \geq 22$) states, this distribution in the single collision limit can be approximately characterized by a Boltzmann distribution with T = 1030 ± 30 K. The distribution in the lower rotational states approximates even higher temperatures. The different rotational distributions suggest that these two vibrational channels have different reaction mechanisms, possibly a more direct reaction for v = 0, and a more intimate collision for v = 1. It is also observed that high rotational states of $CO^+(v=1)$ are more rapidly relaxed on collisions with CO than lower states.

35A

Metal Cluster Chemistry: Surface Reactions at the Molecular Level*

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For the first time it is possible to study the gas phase chemical reactions of small clusters of metal atoms. From a chemical point of view, reactions of metal clusters bridge the gap between reactions of individual metal atoms and those involving bulk metal. It is expected that studies of these microscopic aggregates (2-200 atoms) will provide additional insight into surface chemistry at the molecular level. By combining a laser vaporization cluster source with a continuous gas flow reactor, we have conducted a comprehensive study of the chemisorption of hydrogen (deuterium) on iron clusters. The results of these experiments will be used to illustrate the transition from molecular to bulk behavior as cluster size increases. In particular, the following aspects of the hydrogen (deuterium) chemisorption on iron clusters will be examined in detail: (1) cluster reactivity through kinetic studies of H_2 (D_2) addition; (2) structural implications through studies of the composition of fully hydrogenated clusters; (3) chemisorption energetics through laser-induced desorption experiments; and (4) catalytic behavior of metal clusters through H/D exchange measurements. Studies of iron cluster reactivity with several other molecules will also be presented.

*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under Contract W-31-109-ENG-38.

35B

The Dependence of Reaction Cross Sections on Reagent Rotation

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Integral cross sections of the two endothermic reactions

$$Na + HF\ (v = 1,j) \rightarrow NaF + H \quad (\Delta D_0{}^0 = 0.54\ eV)$$

$$K + HF\ (v = 1,j) \rightarrow KF + H \quad (\Delta D_0{}^0 = 0.8\ eV)$$

(v,j = vib, rot states) have been measured for j = 1 to 6 at various translational energies E ranging from 0.5 to 0.9 eV (Na + HF) and 0.7 to 0.9 eV (K + HF) using the crossed molecular beam method. Measurements for the reaction Li + HF (v = 1,j) → Li F + H are currently being performed. First results will be presented at the conference.

The reaction products emerge from the intersection volume of a continuous (alkali) and a pulsed (~ 100 µs) nozzle beam. The pulsed molecular beam source is synchronized to a pulsed chemical HF-laser which is tuned to one of the $P_1(j+1)$-lines of HF. A few mm upstream from the reaction volume the laser beam crosses the particle pulse perpendicularly and excites a fraction of the molecules to the desired v = 1,j-state. The intensity of scattered particles is measured by a Langmuir-Taylor-detector (Re-ribbon) positioned to the most probable centroid angle. The detailed integral reaction cross sections $\sigma_r(j;E)$ are then proportional to the difference of signal transients for laser "on" and "off" devided by the measured intensity of the spontaneous infrared radiation emitted by the HF-molecules.

It was found that for the both reactions the cross sections first decrease slightly with increasing j, pass a faint minimum at j = 3 or 4 and increase again. The initial descent becomes weaker with increasing E while the final rise grows more marked for Na + HF and less steep for K + HF.

The results will be interpreted in terms of a novel "sliding mass"-model which clearly illustrates the tight correlations between the j-dependence of $\sigma_r(j;E)$ and the anisotropy of the potential energy surface. According to the model a steep descent of $\sigma_r(j;E)$ with rising j - as observed for K + HCl [1] - is likely to be due to an anisotropy characterised by a cone of acceptance with small cone angle while the shape of the present results reflect a wide cone angle. Furthermore, the model strongly suggests that the spectacular structure of $\sigma_r(j;E)$ (E = 0.38 eV) predicted for Li + HF (v = 2,j) → LiF + H in a quasi classical trajectory study [2] based on the Carter and Murrell potential energy function [3] is completely due to the unrealistic angular dependent features of the surface occuring at large reagent separations.

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35C

Differential and Integral Cross Sections for the Reactions $K + HCl, HBr \rightarrow KCl, KBr + H$

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Although these reactions are among the first ones ever studied in molecular beam experiments only little is known about their differential cross sections. There is one investigation on K + HBr [1] (collision energy E = 0.12 eV) but none on K + HCl. The main reason for this lack of data is the unfavourable mass ratio of the products which confines the detected salt molecules closely to the centroid angle. As a consequence, the angular distributions of products measured in the scattering plane are dominated by the velocity and angular distributions of the parent beams and contain only vastly averaged information about the center-of-mass (cm) cross sections. However, out-of-plane distributions are only little affected by the beam spreads and reflect directly the recoil velocity distribution of the products. If both types of data are collected the determination of cm-cross section becomes possible.

In a series of crossed molecular beam experiments we measured for both reactions in- and out-of-plane angular distributions of products at various collision energies E ranging from 0.2 eV to 2.1 eV (HCl) and 0.23 eV to 2.9 eV (HBr), respectively. The cm-cross section J has been determined by a standard least square fit procedure assuming that J separates into an angular (ϑ) and velocity (u) dependent function $J(\vartheta,u;E) = f_E(\vartheta)g_E(u)$. For both systems distinct forward scattering (K-direction) has been found at all energies. At the lowest E-values 65 % of the products appear in the forward hemisphere. This contribution becomes more marked as the energy increases and reaches 73 % (HCl) and 80 % (HBr) at the highest energies. The fraction of the energy available to the products which is converted to product translation decreases slowly with rising E from 54 % to 31 % (HCl) and 46 % to 21 % (HBr).

The in- and out-of-plane distributions have been integrated to obtain the integral reaction cross section $\sigma_r(E)$. For K + HBr $\sigma_r(E)$ is almost independent of E within the entire range studied. In case of HCl, σ_r exhibits an initial steep rise followed by a levelling off. The latter shape has been reported previously [2]; it is typical for a reaction with non-vanishing threshold.

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36A

COLLISIONAL DEACTIVATION OF LARGE POLYATOMIC MOLECULES STUDIED BY MULTIPHOTON IONISATION.

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A resonant multiphoton ionisation method has been developed which is suitable e.g. for direct observation of the collisional deactivation of vibationally highly excited polyatomic molecules: With a "selective ionisation by kinetic control" (SIKC) scheme, using properly chosen wavelength and pumping conditions, time delayed photoionisation can be confined to molecules with internal energies of limited ranges. This allows to observe the time evolution of molecular populations in distinct "energy windows" on the vibrational energy scale during the course of collisional deactivation. The resulting data contain information on the average energy removal in collisions and on the alterations of the initial energy distibutions.
Examples are shown and discussed of collisional deactivations of alkylated benzenes and their isomers.
The vibrationally highly excited ground state molecules are prepared via a photochemical reaction step or by an internal conversion following UV excitation into higher singlett states.

36B

Photolysis of $Ar_2(^3\Sigma_u)$ at 308 nm

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The interaction of high energy radiation γ-rays, electrons or protons with inert gases has received considerable attention over the years. The kinetics and energy transfer processes involving excited atomic and molecular metastable states, as well as processes which remove higher lying excited states, serve as simple prototypes for a variety of processes involving Rydberg type atoms and molecules. Such processes are also relevant to the understanding of gas-discharge phenomena and the operation of excimer lasers.

This poster will discuss some recent experimental results on the kinetics of the 4 excited atomic states of Ar of the $3p^5 4s$ manifold $^3P_2$, $^3P_1$, $^3P_0$ and $^1P_1$. These excited states were produced from the photodissociation of Ar_2 ($^3\Sigma^+_u$) at 308 nm in a high pressure Ar afterglow. Pulse radiolysis with a 1 Mev, 50 nsec pulse of electrons into pure Ar at moderate (0.5 to 2 atm) pressure was used to create Ar_2 ($^3\Sigma^+_u$). After a variable time delay from the initial e-beam pulse Ar_2 ($^3\Sigma^+_u$) was photodissociated by a 50 mJ pulse of light at 308 nm. The resulting changes in the population of Ar atoms in the excited $3p^5 4s$ manifold were monitored by atomic absorption spectrophotmetry. Over the pressure range investigated these monitored Ar 4s levels were populated at a measurable rate indicating that energy transfer from the initially produced higher excited atomic levels must take place through the formation and decay of molecular states.

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36C

VIBRATIONAL MOTION EFFECTS ON MOLECULAR POLARIZABILITIES AND HYPERPOLARIZABILITIES AND THE INFLUENCES OF APPLIED ELECTRIC FIELDS AND GRADIENTS

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The dependence of molecular tensor properties on the internuclear coordinate is examined for lithium hydride using the Derivative Hartree-Fock Theory.[1] The variations noted for some polarizabilities were substantial for even small changes in the internuclear coordinate. These properties were then vibrationally averaged over different vibrational wavefunctions of the ACCD potential energy surface.

Using the appropriate averaged polarizabilities, the vibrational energy levels were calculated variationally for different applied electric fields and field gradients in order to evaluate the contributions of the different order properties and vibrational state. The field gradient along the axial direction was found to play a significant role in shifting vibrational transition frequencies of the molecule. The effects of the induced moments on the dipole transition moments were also investigated as a function of the applied fields.

The impact of these results on the internuclear potential energy surface will be discussed as well as the effects on collisional differential cross sections.

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37A

THE EFFECT OF SURFACE CORRUGATION IN MOLECULE - CRYSTAL SURFACE COLLISIONS

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Classical trajectory calculations of a rigid rotor diatomic molecule scattering from a two-dimensional rigid surface have been carried out. The effect of the corrugation of a repulsive surface on rotational inelasticity and on the polarization behavior of the diatomics has been investigated. It is found that polarization data in good agreement with experiment is obtained only at high corrugation. Addition of an anisotropic attractive potential allows good agreement with experiment for even low corrugation.

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POSTER

37B

Substituent Effects on Chemiionization Reactions in Crossed Molecular Beams

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The mechanisms of a variety of organic chemiionization reactions can be investigated when a supersonic nozzle beam of a Lewis acid (seeded in a lighter carrier gas) reacts with a similar beam of Lewis base. Thus we have looked at proton, electron and halide transfer reactions:

$HI + B \rightarrow HB^+ + I^-$ $\qquad$ $A = SbCl_5$, $SnCl_4$, $TiCl_4$, or SbF_5

$A + B \rightarrow A^- + B^+$ $\qquad$ B = an amine

$RX + SbF_5 \rightarrow R^+ + SbF_5X^-$ $\qquad$ RX = an organic halide

In the first two cases the reaction is direct[1,2] and proceeds by a modified stripping mechanism. The halide transfer reaction proceeds via a long-lived complex[3] (except at the highest energies). This has been established for the cases where $RX = Y\text{-}C_6H_4COCl$, Y = H, o-, m-, p-Cl. Comparison of product intensities at the maximum shows that meta-chlorobenzoyl chloride is the least reactive as expected from the relative energies of the product ions.

The reaction of butyl iodide with SbF_5 might be expected to show rearrangement of the butyl ion on the basis of solution studies.[4] Preliminary results indicate that the threshold for reaction of t-butyl iodide is appreciably lower than that for the primary isomer. We have also recently compared the ease of Cl^- transfer with that of Br^- in the reactions of $Cl(CH_2)_2Br$ and $Cl(CH_2)_3Br$ with SbF_5. The former yields approx. 99% Cl^- transfer, the latter 90%.

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37C

Collisional Redistribution of Resonant Radiation in Intense Laser Fields

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Previously we have studied the pressure broadening and depolarization of the Sr resonance transition in the weak field limit[1]

$$Sr(^1S) + Ar + \hbar\omega_L \overset{\Omega_L}{\rightleftharpoons} Sr^*(^1P) + Ar \overset{\Omega_R}{\rightsquigarrow} Sr(^1S) + Ar + \hbar\omega_R$$

where the Rabi frequency Ω_L for absorption of the incident laser photon $\hbar\omega_L$ is taken to be small. In particular we examined the non-adiabatic effects associated with the degenerate ^1P scattering channel states using close coupling procedures developed for scattering in radiation fields[2] to predict the observed polarization the fluorescent photon ω_R. Since our radiative close coupling codes are capable of treating strong field effects[3] we are now systematically increasing the laser field strength and examining the effects of saturation on the fluorescence spectrum. Three distinct problems associated with such optical collision process are being studied.

(1) The impact limit for optically allowed transitions. Even for the weakest fields, as the detuning $\Delta_L=(\omega_L-\omega_{if})$ of the laser from the resonance frequency ω_{if} of the atomic transition becomes small, we eventually achieve saturation in the close coupling codes. This is indicative of the impact limit in pressure broadening theory. We will show how proper pressure broadened half widths, which include elastic and inelastic effects, can be rigorously extracted from close coupled radiative scattering matrix elements.

(2) Inelastic scattering among atomic dressed states. As Ω_L is increased and eventually exceeds Δ_L the asymptotic channel states for the collision complex Sr + Ar become dressed and the proper scattering boundary conditions must be referenced to the ac Stark shifted states of Sr. Scattering cross sections between these states obtained from our fully quantal close coupling code will be compared to the 4-state semiclassical model results of Light and Szöke.[4]

(3) Collisional redistribution spectra in the impact limit. We have expanded the close coupling code to include a second photon field of frequency ω_R. We introduce a large, nearly resonant Rabi frequency Ω_R for the redistributed photon and calculate the radiative scattering matrix. By scanning through ω_R we obtain the pressure-broadened redistribution spectra in the impact limit and observe manifestations of the typical three-peaked Mollow lineshape due to fluorescence between dressed atomic states.[5]

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38A

RESONANT ROTATIONAL ENERGY TRANSFER IN HF

by

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ABSTRACT

An in plane, crossed molecular beam apparatus has been used to measure resonant rotational energy transfer in collisions between two HF molecules. The primary molecular beam was formed from a 1% HF in He mixture expanded from a source pressure of up to 22 atm. In this way the majority of the HF could be cooled into the J=0 and J=1 states. Individual state populations were measured using an F-Center laser in conjunction with a liquid helium cooled bolometer detector. A pure HF secondary beam was used to attenuate the primary beam while monitoring the individual state populations of the later. The attenuation measurements obtained in this way clearly show effects which can be attributed to resonant rotational energy transfer resulting from the long range dipole-dipole interactions. A kinetic model was used to extract state-to-state cross sections from this data. The first order dipole allowed process HF(J=0) + HF(J=1) → HF(J=1) + HF(J=0) is found to have a cross section of approximately 300 $\mathring{A}^2$. In addition, the results indicate that the second order dipole allowed cross sections, having ΔJ=2, are about 40 $\mathring{A}^2$.

38B

Real Time Measurements of the Infrared Photodissociation of Polyatomic Van der Waals Molecules

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A reflectron type time of flight mass spectrometer with a multiphoton ionization source is used to measure the infrared photodissociation dynamics of polyatomic Van der Waals molecules. The attenuation of a dimer mass peak is monitored as a function of the time delay between vibrational excitation with a CO_2 laser and ionization with the tripled output from a Nd Yag laser. Both weakly bound and hydrogen bonded systems are being studied. Results will be reported.

38C

Pressure Broadening Line Shape Cross Sections of HD Colliding with H_2 and He

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The pressure dependent width and shift cross sections of HD (J=0 → 1) colliding with H_2 (para and ortho) and He have been calculated following the formalism of Ben-Reuven.[1]

The scattering matrix elements contributing for the HD-H_2 system have been derived from a 12-term interaction potential which gave quantitative agreement with beam experiments (J=0 → 1 differential cross sections) of Buck et al.[2] Since the shift cross sections are extremely sensitive to the centrifugal stretching effects of the molecules,[3] but only two intramolecular distances of each molecule have been retained in the potential representation used, and additionally the temperature averaging had to be done for a function of changing sign, we can only present qualitative results for the shift. The results for the width are more reliable. Inelastic effects contributing to the (elastic) cross sections will be discussed.

All the difficulties arising for the molecule-molecule system could be avoided with regard to the HD-He system. The six-term interaction potential,[4] used for obtaining the scattering matrix elements has been tested very successfully,[5] the centrifugal stretching effects are sufficiently represented[4] and, even the missing resonance features are in favor of a straightforward calculation of the cross sections.

In the comparison of both systems, we have found comparable results for the width cross sections but different signs for the shift. Reasons confirming the latter disagreement will be discussed.

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39A

Relative Reaction Rates of Gas-Phase Transition Metal Clusters

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A new fast-flow device has been developed for the study of metal cluster reactions in the gas phase. Metal clusters are produced by laser vaporization of a metal target in the throat of a pulsed supersonic expansion, and expand into a fast-flow reaction tube. Reactants are injected into this tube, mixed by turbulence, and the metal cluster-reactant mixture expands into vacuum as it exits the reaction tube. Direct one-photon ionization with the F_2 excimer laser (157 nm, 7.89 eV) coupled with time-of-flight mass spectroscopy allows the reaction products to be probed.

Relative rates of reaction are determined by the amount the bare cluster signal depletes when reactant is injected (compared to a control experiment with helium injected). Experiments show that the pattern of reactivity of cobalt clusters with D_2 and N_2 is similar, with huge variations in reaction probability as a function of cluster size. Similarly huge variations occur in the $Nb_n + N_2$ and $Nb_n + D_2$ systems, but with a different reactivity pattern than observed for cobalt. In addition, a titration limit is observed for $Co_n + D_2$, in which reaction stops when a certain number of D_2 molecules have been added, leading to species such as $Co_{11}D_{10}$, $Co_{12}D_{10}$, $Co_{13}D_{12}$, $Co_{14}D_{12}$, $Co_{15}D_{14}$, and $Co_{16}D_{14}$. In contrast, reactions between CO and various transition metal clusters show no strong dependence on cluster size whatever.

These dramatic patterns of reactivity of metal clusters provide stringent tests for future theories as to the nature of chemisorption on metal surfaces at a detailed, molecular level. In addition, the reaction tube design produces jet-cooled product molecules which are suitable for spectroscopic study. This will enable the detailed characterization of the metal-ligand bond by high-resolution electronic spectroscopy.

39B

Time-dependent quantum mechanics of the colinear H + H_2 reaction

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The time-dependent Schrödinger equation is used to evaluate the reaction probabilities for the linear H + H_2 reaction. The wave function is written as the product of time-independent translational and vibrational functions and time-dependent coefficients. A minimum wave packet is created from the initial coefficients. The time-dependent Schrödinger equation is then evaluated at a time after the packet has cleared the barrier to obtain the probability of reaction. One attractive feature of this approach is that the integrals are independent of the time and kinetic energy associated with the initial packet. Therefore, they need only be evaluated once for the range of translational energies being considered. Once these integrals have been evaluated, the calculation of the probability takes relatively little computer time. Another feature of this procedure is that in the evaluation of the probability, it is not necessary to integrate the time-dependent equations in a step-wise manner over time. This saves considerable time since only one time step of any size need be used. Calculations are done using both a LEPS(London-Eyring-Polanyi-Sato) and a Porter-Karplus potential energy surfaces to facilitate comparison with previous work.

39C

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We report on recent work involving the application of the classical path method to reactive scattering. The classical path method is a semiclassical method for obtaining transition probabilities which treats some degrees of freedom quantum mechanically and others classically. In applications to reactive collisions, the coordinate system employed must treat the various arrangement channels even handedly. Through the use of hyperspherical coordinates, the "distance" between two interacting moieties, irrespective of their arrangement, may be treated classically while one or more of the remaining degrees of freedom are treated quantum mechanically. Our general approach is outlined in the following paragraphs, and numerical results for the collinear D + HH system are provided.

The full quantum Hamiltonian in hyperspherical coordinates is transformed so that the direct substitution of the relation

$$\hat{P}_q = -i\hbar \frac{\partial}{\partial q} \tag{1}$$

for all coordinates q yields the correct kinetic energy operator. Then the momentum operators corresponding to all degrees of freedom to be treated classically are replaced by classical momentum variables. We treat the hyperradius, ρ, and the three "external" (Euler) angles as classical variables; the two "internal" angles, ϑ and φ, on which the potential depends, are treated quantum mechanically. The resulting "mixed" Hamiltonian has the form

$$\hat{H} = H_{cl} + \hat{H}_0(\vartheta,\varphi,t) + \hat{H}_1(\vartheta,\varphi,t) \tag{2}$$

where the time dependence of $\hat{H}_0$ arises solely through the classical variable ρ, while the time dependence of $\hat{H}_1$ arises through classical variables in addition to ρ.

The (adiabatic) eigenfunctions of $\hat{H}_0$,

$$\hat{H}_0(\vartheta,\varphi;\rho)\,\Psi_n(\vartheta,\varphi,\rho) = \epsilon_n(\rho)\,\Psi_n(\vartheta,\varphi;\rho) \tag{3}$$

are employed as a basis for expanding the total time-dependent wavefunction in the variables ϑ and φ:

$$\Psi(\vartheta,\varphi,t) = \Sigma_n\, a_n(t) \exp\left[-\frac{i}{\hbar}\int^t \epsilon_n(\rho(t'))\,dt'\right] \Psi_n(\vartheta,\varphi;\rho(t)) \tag{4}$$

The time-dependent Schroedinger equation

$$(\hat{H}_0 + \hat{H}_1)\,\Psi = i\hbar \frac{\partial}{\partial t}\Psi \tag{5}$$

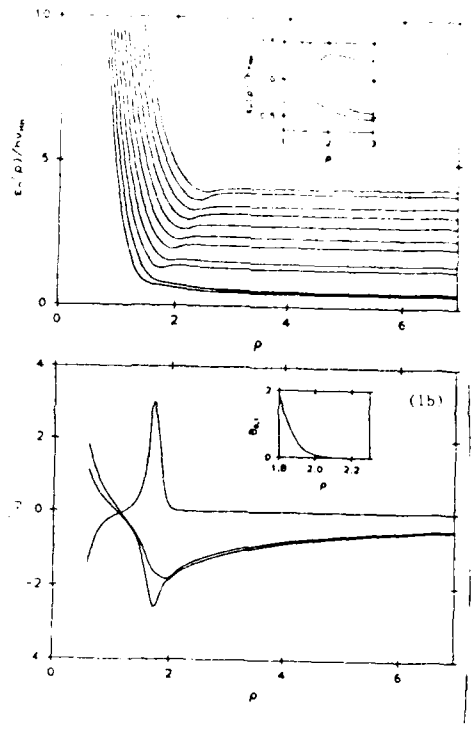
provides the equation governing the time derivatives of the amplitudes in Eq. (4).

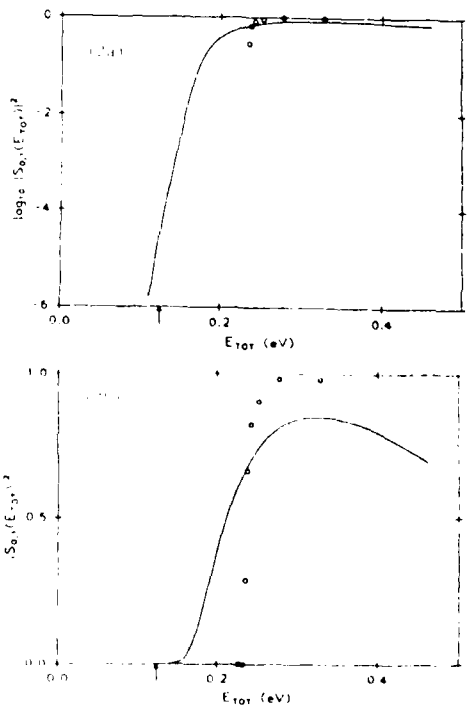
The equations of motion of the classical variables are obtained from the semiclassical Hamiltonian

$$H_{sc}(\rho,P_\rho,\vartheta,P_\vartheta,t;J) = \frac{1}{2\mu}P_\rho^2 + \Sigma_n |a_n(t)|^2 \epsilon_n(\rho) + \langle \hat{H}_1 \rangle \tag{6}$$

which is the expectation value of the "mixed" Hamiltonian operator in Eq. (2) using the time-dependent wavefunction in Eq. (4). The requirement that $dH_{sc}/dt = 0$ gives rise to an additional "force of constraint" in the equation for $\dot{P}_\rho$.

As an example of this approach, we examine the collinear D + HH reaction on the Porter-Karplus potential. Figures 1a and 1b show the adiabatic potential energy curves from Eq. (3) and the nonadiabatic coupling elements, respectively. Note that the coupling between different arrangement channels vanishes for ρ larger than some small value characteristic of the strong interaction region. In contrast, the coupling within a given arrangement channel goes as $1/\rho$ at long range. Figures 2a and 2b show the energy dependence of the reaction probability on logarithmic and linear scales, respectively. Also shown are points corresponding to the quasiclassical trajectory results on the same surface.





The classical path method is seen to yield accurate results for inelastic scattering in the limit of weak collisions, as we could expect. The present formulation is most accurate in the low energy region of the reaction. In contrast, only the reverse, [illegible] expected, that the quasiclassical trajectory method cannot treat it accurately. The two methods may prove to be complementary. [illegible] is in progress.

40A

Poster to be presented at the 1985 Conference of the Dyanmics of Molecular Collisions, Snowbird, Utah.

STATE-TO-STATE VIBRATIONAL RELAXATION IN $^1B_{2_u}$ BENZENE-d_6 INDUCED BY LOW ENERGY COLLISIONS.

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Vibrational relaxation in S_1 benzene-d_6 has been explored using time-resolved, state-selected, dispersed fluorescence spectroscopy. Pathways for collisional deactivation of the level 6^1 have been mapped for collisions with argon in the translational temperature regime 1 - 20K. Low energy collisions induce transfer predominantly to the levels 11^1, 16^1 and 16^2. Relative rates for each of the individual relaxation channels have been measured as a function of the mean collision energy (corresponding to the relevant translational temperature). The data comment on the issue of resonance enhancement of vibrational relaxation cross sections at low collision energies and on the collision energy dependence of state-to-state propensities in polyatomic vibrational relaxation.

40B

Recombination Reactions of van der Waals Molecules

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In previous work it was demonstrated that reactions of van der Waals molecules and clusters may provide a useful medium for studying the effect of the "third body" on chemical reactions. It has been shown that even a single "spectator" which is involved in the process can effectively induce new types of phenomena.

It is of course of special interest to investigate reactions that can not occur between two species, and for which the "third body" is really essential. In the work that is here presented, we concentrated on such a process - namely recombination reactions for which the spectator is needed in order to carry away some energy from the reaction complex, thereby stabilizing it. The reactions studied were: $O(^3P) + CO \cdot R_n \rightarrow CO_2^* + \ldots$ and $O(^3P) + NO \cdot R_n \rightarrow NO_2^* + \ldots$; where R are the spectators Ar, Ne, He, N_2, CO_2, SO_2 and CO/NO, and CO_2^* and NO_2^* are the electronically excited products.

Applying the cross-molecular atomic beam technique and detecting the total chemiluminescence signal from the products, as well as its angular distribution and velocity, new insight on these processes could be gained.

Because of the sensitivity of the reaction cross-section to the number of spectators, the technique was proven to be a sensitive measure for the clusterization process.

40C

MODIFICATION OF THE HINDERED-ROTOR APPROACH BY MEANS OF LEAST-SQUARES COORDINATES

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The work starts from studing the relationship between Marcus' natural collision coordinates s,n,m [1], the least-squares set of coordinates $s^{(ls)}$, $q_{\parallel}, q_{\psi}, q_{\varphi}$ [2] and their Cartesian analogue used by Miller, Handy and Adams [3] for a collinear reaction AB+C→A+BC. It is shown that compared with Marcus' reaction coordinate s the use of the least-squares reaction coordinate $s^{(ls)}$ [2] provides better separation between overall rotations and the bending motion along the reaction path which is chosen to be exactly the same in the two cases. (Note the difference between the terms "reaction path" and "reaction coordinate".) The essential point is that different reaction coordinates result in different bending harmonic frequencies along the path.

The main purpose of the work is to transfer some ideas from the Marcus-Wyatt hindered-rotor approach [1,4] to the formalism based on least-squares coordinates. As a new application a triatomic system dissociating or predissociating on a single potential surface is considered. The torsional angle γ_{eff} is introduced in such a way that near any point at the reaction path it describes the normal vibration with amplitude becoming larger and larger during the dissociation process; at the limit of isolated products the vibration turns into free rotation of the atom about the diatom.

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41A

SPECTROSCOPY AND AUTODETACHMENT DYNAMICS OF NEGATIVE IONS

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The study of autodetaching states of negative ions leads to an understanding of the spectroscopy of these ions as well as the dynamics of the autodetachment process. Using a coaxial laser-ion beam spectrometer, we have obtained an infrared vibration-rotation spectrum of NH^- and an electronic spectrum for CH_2CN^-. In NH^-, transitions between the v=0 and v=1 vibrational levels were pumped with an F-center laser, and subsequent vibrational autodetachment from the v=1 level was detected. In CH_2CN^-, an electronic state near the photodetachment threshold was probed. This is expected to be a dipole-bound state, and the rotational levels above the detachment threshold decay by rotational autodetachment. The NH^- results are particularly interesting as they show markedly different autodetachment lifetimes for the v=1 Λ-doublet levels.

41B

Fraction of Laser Excited Atoms in Na Vapor and Fast Na Beams*

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A beam-gas technique involving ion-pair production in alkali-halogen collisions has been used to measure the fraction, f^*, of laser excited Na atoms, Na^*, in Na vapor and fast (keV) Na beams. The Na^*, which is in the $3^2P_{3/2}$ state, is produced by a Coherent 599-21 single frequency CW dye laser pumped by a Coherent Innova-5 Ar ion laser. In the excited-beam experiments the laser light is coincident with the Na atom beam. The f^* is determined by passing the beam through a vapor of I_2 in a cell and measuring, with the laser on and off, the Na^+ current resulting from the ion-pair production reaction $Na + I_2 \rightarrow Na^+ + I_2^-$. The technique works because the crossing radii are quite different for ground-state (GS) Na and Na^* and allow only the former to react. As an example, for a 5000 eV Na beam and an optimum laser power of 100 mW/cm^2, $f^* \approx 0.065$. In the excited-vapor experiments the pressure in the Na cell is typically 0.1 mTorr. A few keV Cl beam coincident with the laser is used to measure f^* via, as before, ion-pair formation. In this case Cl^- is detected from $Na + Cl \rightarrow Na^+ + Cl^-$. If n_0 is the constant GS Na atom density and $n^*(x)$ the variable Na^* density along the axis x of the cell of length L, then f^* is defined as $f^* = (n_0 L)^{-1} \int_0^L n^*(x)\,dx$. A typical $f^* = 0.02$ for a laser power of 1000 mW/cm^2.

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41C

IMPACT PARAMETER DEPENDENCE OF CHEMICAL REACTION: Opacity function for the Ba + HI → BaI + H system.

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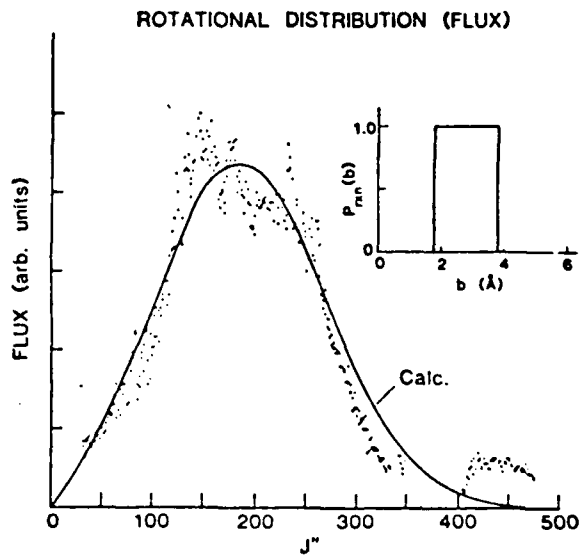
In general, the impact parameter, b, can not be measured experimentally. However, when a heavy atom(**H**) reacts with a heavy-light(**HL**) diatomic molecule to produce a heavy-heavy(**HH**) diatomic molecule, the orbital angular momentum of the incoming collision partners, $L = \mu v_{rel} b$, is channeled into the rotational angular momentum of the product.[1] Therefore, by measuring the rotational distributions of the product **HH** in a specific vibrational level, the impact parameter dependence of the reactive scattering (opacity function) can be determined.

We measured the product rotational distribution in the beam-gas reaction of Ba + HI → BaI(v=8) + H, a near limiting example of such **H+HL → HH+L** reactions. By assuming various shapes for opacity function and by simulating the rotational distributions using a Monte-Carlo method, we obtained the opacity function as P(b)=1 for 1.75≤ b ≤3.75Å, and P(b)=0 otherwise (see Figure).[2, 3] This suggests that the product vibrational level is closely related with the impact parameter. Experiment is under way to determine opacity functions for different vibrational levels of BaI and to understand the relation between the impact parameter and product vibrational distributions.



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42A

DISSOCIATION OF HD BY CONTROLLED ELECTRON IMPACT: ISOTOPE EFFECTS

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HD is the simplest heteroisotropic diatomic molecule and isotope effect in dissociation is likely to be most pronounced.

The lineshape and intensity of Balmer emission produced in e-HD collisions were measured and ratios of the emission cross sections of H*(n=3-7) and D*(n=3-7) were obtained. The results are shown in Figs. 1 and 2.

In the case of n=4, there is a weak isotope effect ($\sigma_D/\sigma_H \sim 1.1$) at 25 eV. It decreased with increasing electron energy up to 45 eV and then increased. This result indicates that a slow component of the excited hydrogen atom[1] (threshold ~ 17 eV, translational energy 0-2 eV) and a fast component (threshold ~ 45 eV) are responsible for the observed isotope effect. Meanwhile in the case of n=3, no isotope effect was observed at all electron energies.

Coupling with the motion of nucleus induces the coupling between gerade and ungerade states and results in an appreciable isotope effect in the dissociation for a slow atom,[2] as is shown experimentally. The isotope effect is expected to be small for a fast atom; the experimental result is, however, contradictory.

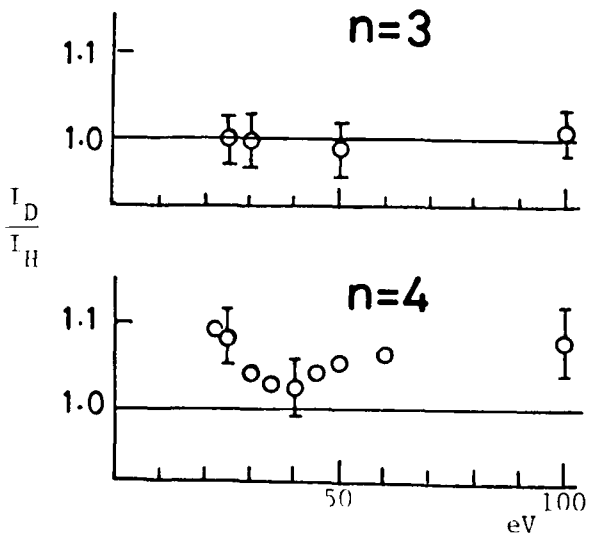

Fig. 1. Relative emission intensity for n = 3 and 4.

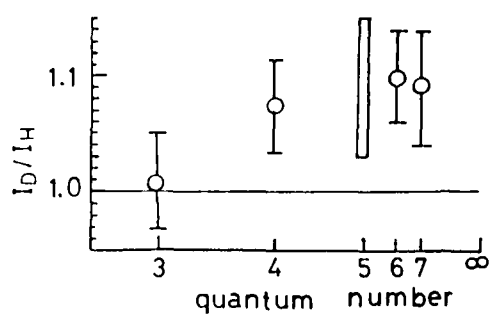

Fig. 2. Principal quantum number dependence at 100 eV.

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42 B

NEAR-RESONANT CHARGE-EXCHANGE IN GAS-SURFACE COLLISIONS: THE THREE ELECTRONIC STATE SYSTEM

by

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A recently proposed theoretical description of near-resonant charge-transfer processes occurring in gas-surface collisions is applied to a system with three electronic channels. The description is based on representing the surface with a small cluster of atoms. A molecular orbital (MO) treatment (Diatomics in Molecules) is used to construct the eigenvalues and eigenfunctions of the surface. These are combined with the corresponding atomic eigenvalues and eigenfunctions of the gas to construct well defined gas-surface interaction potentials and electronic coupling terms. These potentials and couplings are used in the transformation to the diabatic electronic representation. These diabatic potentials provide the input that is needed in the common eikonal formalism. This formalism results in a coupled set of first order differential equations in time which self-consistently determine the evolution of the "nuclear" and electronic variables. These equations have the form of Hamilton's equations of motion with the real and imaginary parts of the transition amplitudes as well as the nuclear "position" and "momentum" forming a set of canonical variables. Integrating these equations leads to a time dependent description of the scattering event.

The formalism is applied to a thermal energy sodium atom scattering from a W(110) surface. The surface is represented by a cluster of five W atoms. The MO procedures lead to fifteen interaction potentials, five of which are asymptotically neutral and ten asymptotically ionic. For a particular choice of the sodium approach, symmetry restrictions reduce the number of electronic states that couple. Results for the ionization probability are presented for the case of three electronic channels. The channels consist of a neutral state (the initial channel) and two ionic states. A comparison with the two state case (one neutral and one ionic) is made to determine the effect of the extra ionic channel. The dependence of the ionization probabililty on the ionic well depth is also investigated.

42C

Variational Transition State Theory for a Radical Combination Reaction on an Ab Initio Potential Energy Surface : $H + CH_3$

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B3H 4J3

Canonical variational transition state theory calculations have been performed for the reaction

$$H + CH_3 \rightarrow CH_4$$

on an ab initio potential energy surface due to Duchovic, Hase and Schlegel[1]. The two rotational degrees of freedom of CH_3 which become vibrations in CH_4 were treated both as harmonic oscillators and as hindered rotations in the transition state. Other vibrations were treated as harmonic. The resulting energy levels and partition functions were compared to empirical rules. Changing from harmonic oscillators to hindered rotations changed the partition functions by an order of magnitude or more for C...H distances greater than 0.3 nm. The C...H distance for the critical complexes was 0.23 nm at 2000K for both models, but 0.28 nm for harmonic oscillators and 0.4 nm for hindered rotors at 300K. For both models, the rate constant is predicted to decrease with increasing temperature.

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43A

NEAR-RESONANT E-V ENERGY TRANSFER FROM THE 2.3 μm ELECTRONICALLY EXCITED STATE OF PuF_6 TO H_2 AND HF[a]

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ABSTRACT

Near resonant electronic to vibrational (E-V) energy transfer from the 2.3 μm electronically excited state of PuF_6 to H_2 and to HF is observed via laser-induced fluorescence (LIF) measurements. In the H_2 case, the LIF displays an interesting rapid decay followed by an anomalously long tail, indicating that the H_2 (v=1) state is serving as an energy storage reservoir. In the HF case, the E-V energy transfer leads to rapid quenching. Emission from the E-V produced HF (v=1) is also observed and found to be strongly absorbed by the HF (v=0) present. This self-absorptioon and the kinetics of both systems have been modeled and the E-V and quenching rate constants determined.

a) Work performed under the auspices of the U.S. Department of Energy.
b) Chemistry Division, MS J567.
c) Theoretical Division, MS J569.
d) Materials Science and Technology Division, MS E505

43B

Molecular beam studies of reactions of Cu with halogens

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The abstraction reactions $Cu + X_2 \rightarrow CuX + X$ for X = F, Cℓ, Br, and I have been studied using electronic chemiluminescence and cw laser induced fluorescence of CuX in order to determine the detailed partitioning of energy in the products. Specific reactions are assigned to Cu ground state (^2S) or excited states (^2D) using the dependence of the signal on the Cu oven temperature. Spectral simulations indicate that vibrational distributions of CuX formed from Cu(^2S) generally decrease with increasing v. This may be attributable to randomization of energy in a CuX_2 collision complex. Total chemiluminescent cross sections are much larger for reactions of Cu(^2D) (~ 6.4Å^2 with Br_2, ~ 4.1Å^2 with I_2, and ~ 1.6Å^2 with $C\ell_2$) than for reactions of Cu(^2S) (~ 0.01Å^2 with F_2 and energetically forbidden with the other halogens). One possible explanation of these favorable chemiluminescent pathways, though largely non-adiabatic, is that ionization of Cu(^2D) during the reaction involves a ^3D $3d^94s$ state of Cu^+ which resembles the electronic structure of the chemiluminescent states. Ionization of Cu(^2S) is not expected to yield excited states of CuX since it involves only the ^1S $3d^{10}$ state of Cu^+, which resembles the ground state of CuX.

43C

VIBRATIONAL ENERGY TRANSFER IN COLLISIONS BETWEEN TWO DIATOMIC MOLECULES: AN APPROXIMATE TREATMENT

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The exact quantum mehcanical study of vibrational energy transfer can quickly become prohibitively time consuming as the complexity of the collision partners increases. This fact has motivated much work in approximating the exact collision problem. A series of sudden approximations has recently been presented (the vibration/rotation infinite-order sudden approximation; VRIOSA) which removes all coupling from the differential equations describing an atom-molecule collision system and has been applied to heavy molecule-light atom collinear, breathing-sphere and full three-dimensional collisions [1]. The VRIOSA results have been sufficiently accurate and computationally convenient to warrant further applications.

Preliminary work is reported here for collisions between two diatomic molecules. Not only is this system a logical extension of the previous work, but also the study can address some of the questions raised regarding the validity of sudden approximations in describing two colliding diatomic molecules [2]. The VRIOSA equations have been derived in three-dimensions even though this initial investigation is restricted to collinear collisions since exact results with which to compare already exist [3]. In the collinear case, one may consider three possibilities in applying the vibrational part of the VRIOSA:

1. approximate the vibrational motion of molecule 1, but not 2,
2. approximate the vibrational motion of molecule 2, but not 1,
3. approximate the vibrational motion of both molecules.

These choices are all considered [4].

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44A

'A Study of Adiabatic and Sudden Approximations for Reactive Collisions'

by

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Absract.

Traditionally, the reactive sudden approximation was used to predict cross sections from the ground rotational state of reactants only. Thermal rate constants were then obtained by assuming that the magnitude of the cross section is the same for all rotational states. Similarly, the adiabatic BCRLM approximation was used to provide approximate cross sections for reaction from the ground rotational state. The discrepancies between the two types of approximation were very large. The adiabatic theory predicted larger thresholds for reaction than the sudden. Above threshold though, the BCRLM cross sections were much larger than the sudden. In the present study, we reformulate both approximations and obtain from them rotationally averaged cross sections. As a result, we find that apart from zero point bend energies, the two theories are in excellent agreement. Numerical comparisons are provided for the energy and (bend) angle dependence of the cross section in the D+HH reaction.

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Semiclassical Wave Packet Studies of Elastic and Inelastic Atom-Surface Scattering from a 3D Model Surface

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The semiclassical wave packet method for the investigation of elastic and inelastic gas-surface scattering is extended to the calculation of diffraction patterns and Debye-Waller factors for scattering from a three-dimensional surface. The methods treats the incident atomic beam as a quantum mechanical wave packet which is propagated by the time-evolution operator through a time-varying potential field produced by the classical motion of the lattice. Application of the method to hydrogen-atom scattering from a model 3D surface yields energy transfer coefficients in good accord with our previous 2D semiclassical results and with the experimental molecular beam data. The calculated final-state momentum and energy distributions are highly structured and show that inelastic effects dominate the scattering process at high surface temperatures. At $T_s = 300$ K, the scattering is found to be more nearly elastic. The structural features of the distributions are shown to be correlated with the power spectrum for the lattice motion. Diffractive scattering is evident even at $T_s = 1500$ K. At $T_s = 300$ K, the diffraction is much more pronounced due to the increased elasticity of the collision and a larger Debye-Waller factor. The positions of the calculated diffraction peaks are found to be in excellent accord with that expected from the known grating and distribution of incident wavelengths. The dependence of the computed Debye-Waller factors upon T_s, the surface Debye temperature and the gas-surface potential well depth is found to be accurately described by the simplified expressions developed by Beeby and by Comsa et al. In general, the method is shown to be well-suited to the study of elastic and inelastic gas-surface scattering.

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44C

Monte Carlo Random Walk Study of Recombination and Desorption of Hydrogen on Si(111)

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The recombination/desorption of H_2 and the desorption of hydrogen atoms from a Si(111) surface have been investigated using Monte Carlo transition-state theory methods with a biased random walk. Rate coefficients, activation energies, pre-exponential factors and angular desorption distributions have been computed for both reaction channels. The distribution of polarization angles for the H_2 rotational angular momentum vector is also reported. The potential-energy surface is expressed as the sum of a lattice potential, a lattice-adatom interaction term, and an adatom-adatom interaction. Keating's formulation as given by Weber is used for the lattice potential. A pairwise sum of 60 Morse potentials represents the adatom-lattice term. The adatom-adatom interaction is a Morse function multiplied by a hyperbolic switching function. The potential parameters are adjusted to fit the theoretical data for the Si(111)-H interaction potential and the measured adsorption energy of H_2 on Si(111). The surface predicts a barrier of 0.61 eV for H_2 adsorption and the existence of an H_2^* precursor state in the recombination/desorption process. Thermal desorption of hydrogen atoms is predicted to be too slow to be an observable process. The computed activation energies are in good agreement with the experimental data. The calculated pre-exponential factor for H_2 recombination/desorption is a factor of 10^3 smaller than the measured results. A detailed treatment of a reaction mechanism involving an H_2^* precursor intermediate indicates that this difference is due to to differences in the surface coverage present in the calculations and in the experiments. In general, the theoretical methods are shown to be well-suited for the study of this type of rare-event process.

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45A

QUANTUM ERGODIC PROPERTIES OF THE HENON-HEILES SYSTEM

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Although semiclassical ergodic theory[1] identifies the consequences of classical ergodicity for quantum systems, it applies only to systems with infinitesimal $\hbar$ which become strictly ergodic as $\hbar \to 0$. The present work[2] investigates the degree to which this theory can be generalized to identify the consequences of possibly incomplete classical ergodicity for quantum systems that are away from the classical limit.

To extend the existing theory, a quantity F_A^{cl} is introduced to measure the degree to which a given property A is a classical constant of motion. F_A^{cl} always lies between 0 and 1 and can be used to define the degree of ergodicity of the classical system. For a system that is strictly ergodic, $F_A^{cl} = 0$ for all "acceptable" A. Next, in a manner inspired by the semiclassical theory, an analogous quantity F_A^{qm} is introduced to measure the extent to which A is a quantum constant of motion. F_A^{qm} approaches F_A^{cl} in the classical limit and, like F_A^{cl}, always lies between 0 and 1. This quantity can be used to define the degree of ergodicity of a quantum mechanical system but this definition becomes precise only as $\hbar \to 0$.

F_A^{qm} and F_A^{cl} are compared for a variety of properties A for the standard Henon-Heiles system with $\lambda = 0.1118$. These studies reveal that the increased classical degree of ergodicity of this system at high energies is mirrored quantum mechanically and has consequences for certain matrix elements. There are, however, some significant differences between F_A^{qm} and F_A^{cl} which may indicate differing degrees of quantum and classical ergodicity. The sources and implications of this disagreement are investigated by examining time-dependent correlation functions of A.

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45B

Scaling Principles in Classical Collision Dynamics

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Abstract

The use of scaling or factorization principles in inelastic molecular dynamics is current. Within a classical description of the scattering process the existence of scaling principles permit the expression of post-collision variables in terms of pre-collision variables through simple polynomial forms. A variety of applications has shown the utility of such a classical scaling theory in reducing computational effort. Interpolation through scaling is extremely accurate and large numbers of trajectory computations can be bypassed.

Correspondence between classical and quantum scaling theories allows for expression of classical scaling coefficients in terms of (state-to-state) quantal transition probabilities. This leads to a new method of inverting classical moments to get quantum information in bimolecular collisions.

The theory is derived for asymptotically integrable systems. It however remains valid for weak perturbation, i.e. for the regular regime in nonintegrable systems. Departures from scaling provide a new means of characterizing the effects of chaos.

A similar scaling also exists for the primitive semiclassical eigenvalue spectrum of typical vibrational Hamiltonians. This effects a simple quantization method wherein it is unnecessary to find any particular EBK torus in order to obtain eigenvalues.

45C

QUANTUM-RESOLVED GAS SURFACE SCATTERING: AMMONIA FROM TUNGSTEN

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Catalysis and corrosion represent an industrially and scientifically important class of heterogeneous processes in which energy transfer at the gas-surface interface plays a fundamental role. Using laser multi-photon ionization spectroscopy, we have obtained the first quantum resolved spectrum of a polyatomic molecule, NH_3, scattered from a surface. Ammonia has been chosen due to its interesting surface chemistry and because it possesses additional internal degrees of freedom (3-axis rotation and inversion) not found in linear molecules (e.g. NO, CO). These experiments consist of scattering a spatially and temporally defined pulsed-supersonic molecular beam of NH_3 from a well-characterized tungsten target under ultra-high vacuum conditions. We have examined NH_3 rotational energy accommodation from both clean and chemically modified surfaces. Concurrent with these studies we have investigated the NH_3 surface residence time with 20 μsec resolution. The results of these experiments and their implications will be presented.

*This work performed at Sandia National Laboratories, supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

46A

MOLECULAR DYNAMICS STUDY OF OPTICAL COLLISION SPECTRA

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The absorption of nonresonant photons outside the impact region of a spectral transition occurs during collisions with the perturber gas. Particularly interesting is the aspect of a spectroscopic investigation of the collision dynamics by the information contained in the intensity and polarization of the fluorescence after a far-wing excitation of collision pairs. In the limit of zero-perturber pressure the observables are directly related to the frequency-dependent optical collision cross sections.

Recently we have made much progress in developing the quantum methods to calculate optical collision spectra. As an example, Fig. 1 shows the thermal-averaged relative fluorescence intensity from the two D-lines following far-wing excitation of Na-Ar collision pairs. From the analysis of the calculation a clear and quantitative picture is derived on the role of the various couplings that determine the final outcome of the collision during the dissociation of the collision pair. For example, the behavior of the D_1 excitation probability at large detunings in the blue wing reflects the energy dependence of a nonadiabatic transition involving the $B^2\Sigma_{1/2}$ and $A^2\Pi_{1/2}$ states (Fig. 2).

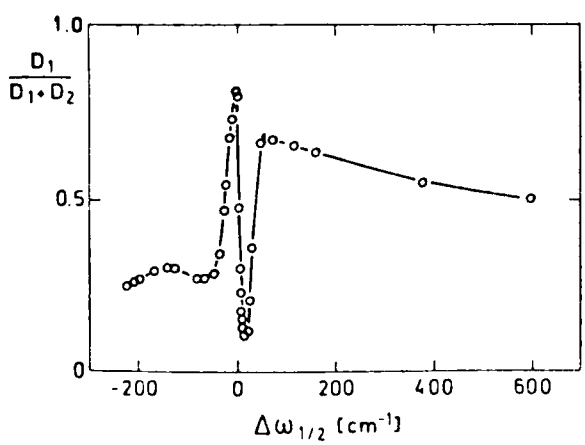

FIGURE 1 Calculated relative D_1 excitation probability versus detuning from the Na-D_1 line.

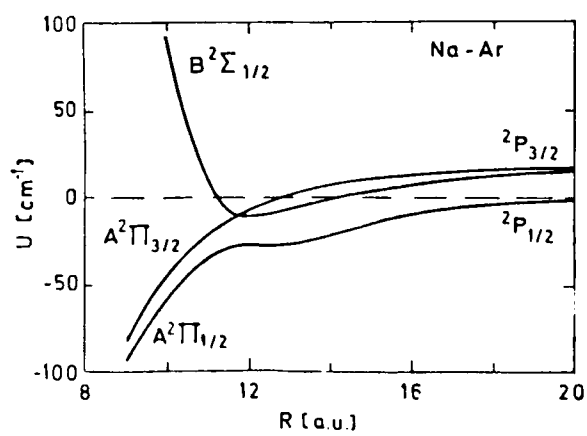

FIGURE 2 Long-range behaviour of the excited Na-Ar potentials

46B

CLASSICAL TRAJECTORY SIMULATION OF THE CHARGE EXCHANGE REACTION

$$Ar^+(^2P_{3/2}) + N_2(^1\Sigma_g, v=0) \rightarrow Ar(^1S_0) + N_2^+(^2\Sigma_g, v')$$

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Classical trajectory calculations have been performed on ad hoc potential surfaces for the named reaction. The potential surface for the entrance channel is obtained from electrostatic parameters and the well depth adjusted to fit experimental results for unreactive elastic and inelastic collisions. The potential surface for the exit channel is obtained from electrostatic parameters and experimental results for the reverse reaction. Surface hopping models are then used and adjusted to investigate the nature of the reactive coupling which produces energy and angular specific scattering of the vibrationally excited products.

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46C

COLLISION-INDUCED ABSORPTION SPECTRA OF H_2-HE AT TEMPERATURES UP TO 100 K.

by

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The recently tested ab-initio potential of H_2-He[1,2] has been used for calculating scattering wave functions representing partial wave expansions for a large set of energy points. Subsequently, the induced dipole moment of the H_2-He system recently determined in ab initio calculations has been used for obtaining dipole transition matrix elements and absorption spectra of various temperatures up to 100 K. Some structure showing up in the spectra is partly due or enhanced by the anisotropy of the interaction potential. One single term (D_{01}) of the dipole moment expansion provides a quasi-thermal component to the spectrum. Its temperature dependence is carefully discussed. The findings of this paper will be compared with results shown in a recent paper of Birnbaum et al.[3] who had published a comparison of measured and calculated spectra obtained in an approximate procedure.

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47A

Time Delay in Classically Forbidden Processes

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We examine the question of time delay in classically forbidden processes. Rigorous mathematical results are derived which seem to violate the relativity principle independent of the total energy of the problem. This result is discussed in terms of wave equations other than the Schrodinger equation. We address a number of other questions which relate to the form of experimentally prepared wavepackets.

47B

1985 Conference on the Dynamics of Molecular Collisions, Snowbird, Utah, July 14-19

A QUANTUM MECHANICAL STUDY OF ROTATIONAL ENERGY TRANSFER IN HF-HF COLLISIONS

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We present quantum mechanical transition probabilities converged with respect to increasing the basis set for rotational energy transfer in HF-HF collisions with total angular momentum zero. Results are presented for calculations employing several hundred channels. Several different total energies and interaction potentials[1,2] are considered. An important aspect of this work is to determine the best order to add rotational and orbital basis functions for efficient convergence of the probabilities. It appears that larger basis sets are required than were used in previous studies[3] of this problem.

We wish to acknowledge support for this work by the National Science Foundation, under grant no. CHE83-17944, and grants of computer time from the University of Minnesota Supercomputer Institute, the Control Data Corporation, and Cray Research Incorporated.

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47C

A Study of the Reaction $H_2^+(v_0') + H_2(v_0''=0) \longrightarrow H_3^+ + H$ Using the Photoionization and RF Octupole Ion Guide Methods

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Total phenomenological cross sections of the title reaction for individual vibrational state of H_2^+ have been measured previously with the photoionization and the single reaction chamber techniques at center-of-mass collision energies ($E_{c.m.}$) less than 1 eV [1-3]. Since the phenomenological cross sections represent velocity averages over the microscopic cross sections, conversion of phenomenological cross sections to microscopic cross sections is desired in order to compare experiment with theory. However, there are severe practical limitation on the accuracy to which microscopic cross sections may be derived by this means.

We have measured the absolute total microscopic cross sections of the title reaction as a function of vibrational state of H_2^+, $v_0'' = 0$-4, over the $E_{c.m.}$ range of 0.25-15 eV using the photoionization and RF ion guide methods. The experimental results are compared to the "trajectory surface hopping" (TSH) calculation of Stine and Muckerman[4] and the recent quasi-classical trajectory calculation of Eaker and Schatz[5]. The absolute total cross sections measured for $v_0''=0$ and 3 at $E_{c.m.}$ = 0.5, 1, 3, and 5 eV are found to be in better agreement with the TSH calculations of Stine and Muckerman which include diabatic charge transfer. This study and the isotopic study of Anderson et al.[6], together with the recent state-selected study of the symmetric charge transfer reaction $H_2^+ + H_2$ [7], provide detailed experimental data for probing the dynamics of the $H_2^+ + H_2$ reactions.

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48A

Abstract for Snowbird Conference

Rotational Effects on Intramolecular Vibrational Energy Flow in HCN.

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Recent results have shown significant rotational effects on the rate of intramolecular vibrational energy transfer for the local mode model of H_2O (W.B. Clodius and R.D. Shirts, J. Chem. Phys. 81, 6624, 1984). Applying similar classical techniques to the HCN local model, the effects of rotation on vibrational behavior are examined. Poincaré surfaces of section are used to illustrate these results. Classical and semiclassical analysis is used to calculate the rates of energy transfer. These rates will be compared with the experimental spectrum of HCN.

48B

DESIGN AND PERFORMANCE CHARACTERISTICS FOR A NEW TANDEM MASS SPECTROMETER

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A tandem hybrid mass spectrometer has been designed with emphasis on the capability to investigate the collision dynamics of the collisional activation step. The combination of a commercial high resolution mass spectrometer as the ion gun with a supersonic molecular beam which accurately defines the collision region, a deceleration lens which permits the exploration of the energy regime from 0.3 eV-6 kilovolts, and a rotatable spherical energy analyzer with a quadrupole mass filter final detector provides the necessary instrumentation for characterizing CAD collisions dynamically. A third mass spectrometer serves to characterize the neutral beam. The combination of these characteristics permits us to establish the relative importance of competing reaction channels, measure the absolute cross-sections for these reactions with moderate accuracy and evaluate quantitatively the relative importance of such key experimental parameters as reactant collision energy, kinetic energy distributions of the reaction products and their angular scattering properties.

Design features of the instrument will be discussed and preliminary results will be presented. Whether the total instrument is a virtual tandem mass spectrometer or a real one depends primarily on the delivery of crucial components which have been ordered but not received as of the date of this abstract. As a minimum the performance of the deceleration lens, molecular beam and rotatable detector will be presented.

48C

Molecular dynamics of Penning ionization:

Ionization of H_2 and its isotopes by $He^*(2^{1,3}S)$†

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Mass-analyzed kinetic energy dependence of relative cross sections for all possible ionic products for $He^*(2^{1,3}S) + H_2$, D_2 and for $He^*(2^{1,3}S) + HD \rightarrow HD^+$, HeH^+, HeD^+, $HeHD^+$ has been measured in the range E = 0.5-3.0 kcal/mol using a crossed supersonic beams apparatus described briefly elsewhere [1]. The results for total ion production, obtained by summing the signals for contributing channels, are fit within experimental error for both ^1S and ^3S by calculations based on optical potential surfaces [2] obtained from nonreactive scattering of He* by D_2. Product ion branching is currently being analyzed using the turning-point-Langevin model proposed earlier [1]. While the data and the model do not agree perfectly, both disagree with earlier classical trajectory calculations [3], in that we find that the ratio of rearrangement ionization (HeH^+ or HeD^+) to the total declines rather than increases with collision energy, and is tracked by the minor associative ionization (HeH_2^+) channel.

† Supported by the National Science Foundation and by the donors of the Petroleum Research Fund administered by the American Chemical Society.

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49A

ENERGY TRANSFER IN H + CO COLLISION

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The vibrational, rotational distribution of CO resulting from T → V,R transfer in H + CO collisions is measured by VUV Laser Induced Fluorescence. The fast H atoms are produced by photodissociation of H_2S that is pulsed along with CO through a nozzle. The initial rotational state distribution of CO is characterized by a temperature of approximately 60°K. The conditions of the experiments are such that the H atom should have undergone only one collision. The experimental results for H atom translational energy of 2.30 eV are compared with those from trajectory calculations on the HCO surface.

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49B

Adiabatic Switching of Reactive Trajectories

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Trapped, quantized trajectories in chemically reactive systems are efficiently located using an adiabatic switching procedure. We show that certain properties of multidimensional reactive resonances can be understood using these trajectories.

49C

A TWO-POTENTIAL OPTICAL CALCULATION OF e-CH_4 ELASTIC SCATTERING

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Differential cross sections (DCS) for e-CH_4 elastic scattering have been calculated at incident energies of 100, 205, 410, 500 and 820 eV using a two-potential treatment of the first-order static and the second-order polarization-absorption parts of the optical potential correct to second order obtained from a multiple scattering expansion. Using this procedure[1] under reasonable assumptions the direct scattering amplitude can be written as $f_{ST} + f_E - f_{EST}$, where f_{ST} is the scattering amplitude due to the static potential computed using the partial wave method and f_E and f_{EST} are the eikonal amplitudes due to the optical and the static potentials, respectively. f_E and f_{EST} have also been calculated using the Blankenbeckler and Goldberger[2] wave function in place of the usual eikonal wave function. The exchange scattering amplitude has been calculated using the pseudostate local potential method of Vanderpoortan[3] and also using the Ochkur[4] approximation. The DCS have been calculated using (a) only the static and polarization parts and (b) using the static, polarization and absorption parts of the optical potential. The calculated results have been compared with the available experimental data and with oneanother to study the importance of absorption effects at various incident energies. The results will be presented and discussed.

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50A

Reaction dynamics on clusters. The unimolecular decomposition of molecular ions in association with inert gas clusters.

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By carefully controlling the nozzle conditions in the adiabatic expansion of gas mixtures, it is possible to form clusters of the type $Ar_n.X$ and $(CO_2)_n.X$, where X ranges from I_2 to $(CH_3CH_2CH_2)_2CO$. Despite the apparent fragile nature of these mixed clusters, it is observed that upon electron impact ionization X^+ undergoes unimolecular decomposition without significantly disrupting the inert gas component. In some cases the critical energies of reaction are as high as 2eV and several molecular ions display three or more parallel decomposition routes. Examples of these reactions are

$$Ar_n.(CH_3)_2CO^+ \rightarrow Ar_n.CH_3CO^+ + CH_3$$

$$(CO_2)_n.(CH_3)_2CO^+ \rightarrow (CO_2)_n.CH_3CO^+ + CH_3$$

$$Ar_n.(CH_3)_2O^+ \rightarrow Ar_n.CH_3OCH_2^+ + H \rightarrow Ar_n.CHO^+ + CH_3 + H_2$$

From a detailed study of these systems we have been able to draw the following qualitative conclusions regarding the reactions and structure of the $Ar_n.X^+$ clusters [1].

1) In large clusters the ionization and excitation of X appears to proceed via a charge transfer mechanism.

2) The molecular ion decomposes because of the comparatively slow rate of intermolecular energy transfer between it and the inert gas component. Results suggest that the relaxation time for vibrational energy loss from the excited ion to the inert gas component is of the order of 10^{-12} - 10^{-10}s.

3) The molecular ion appears to 'sit on' rather than 'within' the ion cluster.

4) Individual ion clusters appear to exhibit behaviour which could be associated with their undergoing a phase transition.

Results will be presented which indicate that association with an inert gas cluster can modify the decomposition route(s) of a molecular ion.

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50B

1985 Conference on the Dynamics of
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A NEW GLOBAL POTENTIAL ENERGY SURFACE FOR $CH_3 + H_2 \rightarrow CH_4 + H$

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Using reaction-path Hamiltonian methods and variational transition state theory,[1] we have done an extensive analysis of two previously proposed global potential energy surfaces for $CH_3 + H_2 \rightarrow CH_4 + H$, one by Raff[2] and the second a slightly modified version of the Valencich, Bunker, and Chapman surface,[3,4] and we have designed a new surface by improving the Raff surface. Variational transition state theory has been applied to all three surfaces to calculate rate constants. Saddlepoint properties will be compared to previous *ab initio* results,[5] and rate constants, activation energies, and kinetic isotope effects will be compared to experiment. The calculations are also used to evaluate the role of tunneling in this reaction and to determine the properties of the dynamical bottlenecks.

This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences under contract no. DE-AC02-79ER-10425.

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50C

Is DWBA Dead or Alive?; Reactive Scattering Study based on Perturbation Methods (DWBA and CCBA)

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Currently several versions of perturbation methods are available for studying reactive scattering processes. These methods differ in several aspects. Unlike others, in the DWBA method of Salk (Suck)[1,2] the transition matrix elements are expanded in terms of transfered angular momentum, thereby giving additional information on reaction mechanisms by revealing the role of preferential angular momentum transfer. Further the role of asymmetric potential surface in reactive scattering can be understood from the kinematics of transfered angular momentum and its projection. Such points will be explicitly spelled out. Unlike other DWBA treatments, in our DWBA we intentionally maintain the use of unperturbed molecular wave functions in the transition amplitude in order to correctly ensure the important equivalence relation between the prior- and post-forms of interaction, although the perturbed molecular DWBA can be readily implemented into our approach. Any DWBA method which does not satisfy the equivalence relation is subject to strong uncertainty due to indeterminism on the choice of interaction form. Further our DWBA is found to yield nearly identical structures of angular distributions to exact close-coupling calculations unless collision energy is too high[3]. Thus this method enables us to succesfully explore microscopic reaction mechanisms such as the role of angular momentum transfer mentioned above, despite the failure of correct absolute magnitude prediction. Our recently developed more generalized perturbation method of CCBA (coupled-channel Born Approximation) will correct this failure. This point will be judiciously discussed. Further the merit of this method will be discussed by making a comparison with the DWBA method mentioned above. Finally a new theory of reactive resonance scattering will be stressed along the same vein of the perturbation approach that we have presented in various literatures[1-3].

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AD-A161 878 THE CONFERENCE ON THE DYNAMICS OF MOLECULAR COLLISIONS HELD AT SNOWBIRD U..(U) MINNESOTA UNIV MINNEAPOLIS DEPT OF CHEMISTRY D G TRUHLAR JUL 85 AFOSR-TR-85-0930 3/3

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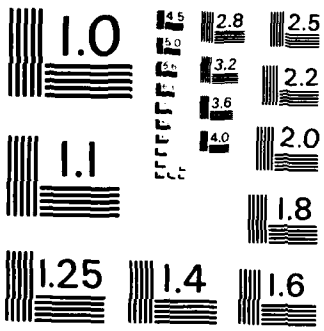

MICROCOPY RESOLUTION TEST CHART
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51A

Applications of the General Classical Variational Theory of the Rates of Atom-Diatom Reactions to the H+HBr Abstraction and Exchange Reactions

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The classical variational theory of chemical reaction rates gives the rate as the equilibrium flux of systems through a trial surface in the phase space of the reaction system(1). The surface divides the phase space into reactant and product regions and is varied to obtain a minimum upper bound for the rate of product formation. For bimolecular reactions of the type A+BC→AB+C, we have derived expressions for the microcanonical and canonical formulations of this theory which give the energy dependent mean reaction cross section $\overline{S}_r(E)$ and canonical rate constant $k_r(T)$, respectively, for the most general surface defined by configuration space coordinates. We have obtained the differential equations which define the best dividing surfaces of this type for both microcanonical and canonical cases. We have developed a numerical method based on a simplex algorithm which permits an efficient determination of the coefficients in the second order expansion of the dividing surface for both the microcanonical and canonical cases.

We have previously applied this method to the $H+H_2$ and $H+I_2$ reactions. These reactions have also been studied by Martin and Raff using a dividing surface defined by a linear combination of the configuration coordinates(2). For these reactions the potential energy surface is symmetrical with respect to attack at either end of the diatomic reactant. Here we apply the method to the H+HBr abstraction and exchange reactions. This reaction system presents a significant challenge to the variational theory. The potential energy surface has a weak angular dependence and dissimilar channels for the abstraction and exchange products, H_2 and HBr, respectively.

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51B

Evaluation of Microcanonical Rate Constants by Path Integral Techniques

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An expression for the microcanonical rate constant that can be conveniently evaluated by path integral techniques is proposed. The efficacy of the method is illustrated by obtaining accurate transmission probabilities as a function of energy for a particle tunneling through an Eckart barrier. The application of the method to systems involving many degrees of freedom is discussed.

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51C

Energy Constraints in the Overtone Vibration Initiated Unimolecular Decomposition of HOOH($5\nu_{OH}$)

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We have extended our studies of the vibrational overtone induced dissociation of hydrogen peroxide (HOOH) and its deuterated analog to the fourth overtone of the OH stretching vibration ($5\nu_{OH}$). This experiment provides a means of investigating the spectroscopy and dynamics of HOOH(HOOD) molecules with increasing amounts of internal energy. The 46.5 kcal mol^{-1} of energy added to the HOOH(HOOD) molecules upon excitation of $5\nu_{OH}$ is 3.1 kcal mol^{-1} less than the dissociation barrier. This dictates that the molecules must possess 3.1 kcal mol^{-1} of initial internal energy to undergo unimolecular decomposition. Detection of rotationally excited OH(OD) products using laser induced fluorescence requires that the molecules have additional energy beyond the minimum required for decomposition. The HOOH excitation spectra change dramatically as the OH level being probed is varied. This reflects the increasing contribution of torsional and vibrational hot bands to the spectra with increasing probe level energy. A model incorporating the different effective torsional potentials in the ground and vibrationally excited molecule describes the coarse vibrational structure in the spectra. In addition the model predicts bands beyond the previously studied region that have now been verified experimentally. A phase space model describing the distribution of the OH(OD) fragments among their rotational states is not consistent with these measurements, unlike the distributions obtained from $6\nu_{OH}$ excitation of HOOH(HOOD).

52A

QUANTUM MECHANICAL THERMAL RATE CONSTANTS

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A formalism for calculating thermally averaged quantum mechanical rate constants for chemical reactions which eliminates the need to solve the state-to-state scattering problem has been previously derived (1). It was shown that the rate constant is the long time limit of the derivative of a side-side correlation function or the time integral of a flux-flux correlation function.

In the present work, we use a basis set expansion method to calculate these correlation functions for a simplified problem. This solution is then used as a reference in a Monte Carlo calculation of the rate constant for the complete problem.

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52B

DYNAMICS OF OH + ALKANE REACTIONS*

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The abstraction of hydrogen atoms from alkanes by OH is the principal mechanism of fuel consumption in lean and stoichiometric alkane/air flames. In this work, kinetic measurements were made on the reactions of OH with protonated and selectively deuterated ethane and propane. These results were combined with theoretical calculations of the geometries, energetics, and thermochemistry of the involved molecular species to produce dynamical information on the reactions.

Figure 1 displays an Arrhenius plot of our kinetic data for the reactions OH + C_2H_6, $C_2H_3D_3$, and C_2D_6. The solid and dotted curves represent, respectively, best-fits of the OH + C_2H_6 and OH + C_2D_6 measurements to equations of the form $k(T) = AT^n \exp-(E/RT)$. The dashed curve is obtained by combining these fits as $k(T) = 0.5[k(OH + C_2H_6) + k(OH + C_2D_6)]$, and provides excellent agreement with our measured data for the reaction OH + $C_2H_3D_3$. These observations are consistent with our theoretical result that the (C-H-O-H) transition state properties are only weakly dependent on the nature of R in the R-(C-H-O-H) activated complex.

Neglecting tunneling corrections, the simplest approximate treatment of kinetic isotope effects considers changes in the activation energy of the reaction brought about by shifts of the zero-point energies in the reactants and activated complex upon isotopic substitution. One would expect $k_H/k_D = \exp \Delta E_o/RT$, where ΔE_o is the reaction activation energy difference caused by deuterium substitution. In Fig. 2, $\ln [k(OH + C_2H_6)/k(OH + C_2D_6)]$ is plotted as a function of 1000/T. Straight-line behavior is observed, $\Delta E_o \approx 910$ cal/mole, and $k_H/k_D \to 1$ as $1000/T \to 0$. These results agree well with our theoretical estimate of $\Delta E_o = 1060$ cal/mole, and suggest that tunneling is unimportant for these reactions at the temperatures studied.

Six OH + deuterium-substituted propane reactions were also studied and are discussed. Separation of reactivity into primary and secondary H-atom abstraction channels was achieved.

* This research is supported by the Office of Basic Energy Sciences, U. S. Department of Energy.

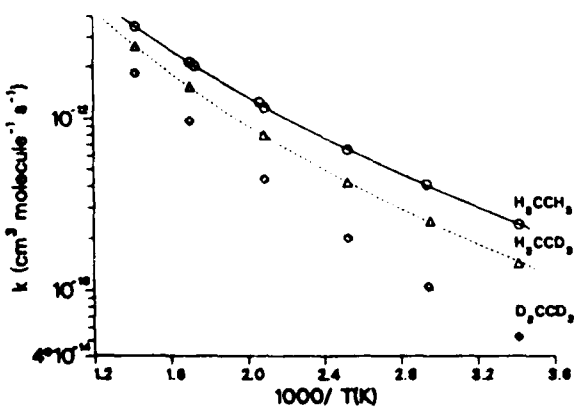

Fig. 1. Kinetic data for OH + ethane reactions.

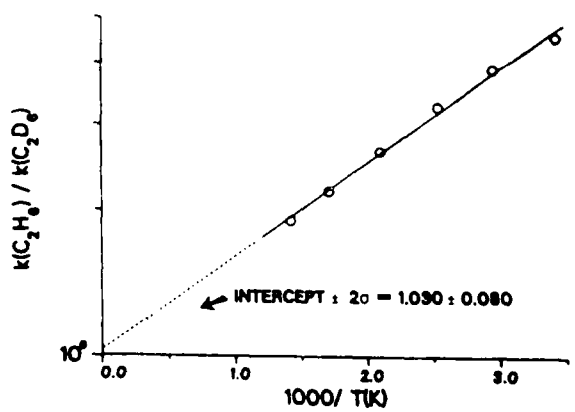

Fig. 2. Kinetic isotope effect in OH + ethane.

52C

Velocity Dependence of Xenon Halide Excimer Rotational Alignment in $Xe^* + RX \longrightarrow XeX^* + R$ Reactions

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In molecular beam experiments, the prefered spatial alignment of an electronically excited molecule can be determined by measuring the polarization of the chemiluminescence. We have recently developed a beam-gas time-of-flight (TOF) method for measuring chemiluminescence polarization as a continuous function of collision velocity. The experiment compares chemiluminescence intensities through an "optical bridge" consisting of two polarizers oriented parallel and perpendicular to the relative velocity vector, v. Since v is fixed in a beam-gas arrangement, this allows us to utilize the TOF method to obtain the rotational alignment over the thermal collision energy range.

We have studied a number of cases involving different halogen donors. In all the cases studied, the rotational alignment is found to depend strongly on: 1) the collision energy, 2) the mass combination (kinematics), 3) the dynamics on the potential energy surface. A situation in which the partitioning of angular momentum is tightly constrained by the conservation laws occurs in the reactions of $Xe^* + HX$ (X=Cl,Br). Both the $XeBr^*$ and $XeCl^*$ excimers have the rotational angular momentum J' strongly polarized perpendicular to v, as expected from the kinematics. While the kinematics alone can satisfactorily account for the polarization of XeX^* from the hydrogen halides, the partitioning of angular momentum is only weakly constrained in the reactions of Xe^* with X_2 (X=Cl,Br,I). In these reactions the observed polarization is thought to be predominately dynamic in origin. This is particularly true for the polarization of $XeBr^*$ from $Xe^* + Br_2$. In this case, the rotational angular momentum vector is seen to show a considerable degree of alignment perpendicular to v. This alignment rapidly decreases as the collision velocity decreases and eventually shows a preference for parallel alignment at the lowest velocities studied. An additional degree of freedom is introduced in the reactions of Xe^* with the halogenated methanes. In these reactions one can investigate the partitioning of rotational angular momentum between the XeX^* excimer and the recoiling methyl fragment. Our results suggest distinct differences in the dynamics of the chloro-, bromo-, and iodomethanes.

At present, calculations employing a version of the direct interaction with product repulsion (DIPR) model are being performed to analyze the dynamic and kinematic contributions to the observed polarization.

53A

Overtone Excitation and Remote Bond Dissociation

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Within the context of unimolecular reactions induced by overtone excitation[2] we present a theoretical study of the intramolecular redistribution of overtone vibrational energy in model chain molecules. We focus on the influence of vibrational mode-mode energy transfer in causing dissociation of the chain at a bond remote from the initial excitation site. Various circumstances that affect this energy flow, such as the presence of a heavy atom blocker in model organometallic compounds, are also studied. In addition to processes describable by classical mechanics, we consider quantal energy transfer as well.

[1]Also associated with the Joint Institute for Laboratory Astrophysics

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53B

A DOUBLE MANY-BODY EXPANSION OF MOLECULAR POTENTIAL ENERGY FUNCTIONS: APPLICATION TO SELECTED TRIATOMIC MOLECULES AND TRIATOMIC VAN DER WAALS MOLECULES

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Recently [1], we have suggested the use of a double many-body expansion (DMBE) of the molecular energy as a means for determining the potential energy functions of small polyatomic systems. The method, which aims for generality by not differentiating between normal molecules and van der Waals molecules, is based on the many-body expansion (MBE) [2] of the molecular energy but treats separately the Hartree-Fock (implied extended-Hartree-Fock whenever appropriate) and the correlation components of the various n-body energy terms; the relevant theory has recently been surveyed [2,3]. Thus, unlike the Hartree-Fock plus damped dispersion energy (HFD) [4] and the Tang-Toennies [5] models of intermolecular forces, breaking of the strong chemical bonds is, of course, allowed within the DMBE formalism.

We report here applications of the DMBE to the ground-state potentials of HeH_2, $HeLi_2$, and HO_2, thus covering surface topographies which range from typical van der Waals interactions to those typically encountered for the ground-state interaction of open-shell systems. The potentials are valid over the complete 3D configuration space of the triatomic system, and show the correct R^{-n} behavior at long-range distances. Thus, they should present no limitations for dynamics studies.

Financial support from the "Instituto Nacional de Investigação Científica" (INIC), Lisboa, Portugal, is gratefully acknowledged.

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53C

THE $Cs(7P) + H_2 \rightarrow CsH + H$ REACTION

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The reaction of cesium atoms with hydrogen is known to be highly endoergic (ΔH 2,7 eV) ; however, by excitation of Cs towards the 7P state, one is able to promote the reaction, although the potential energy which is available above threshold is drastically small, 0.024 eV for $Cs(7P_{3/2})$ and 0.0016 eV for $Cs(7P_{1/2})$.

A supersonic crossed-beam experiment has been built, with laser excitation of Cs atoms and laser detection of CsH molecules ; experimental results are as follows :

- the reaction proceeds after a unique collision between Cs and H_2 has taken place ;
- the $7P_{1/2}$ level is roughly 10 times more reactive than the $7P_{3/2}$ one ;
- the rotational distribution of products in the v" 0 level of the $X\ ^1\Sigma^+$ state of CsH does not depart significantly from the statistical "prior" distribution of Levine and Bernstein ; all the relative kinetic energy which is available can be converted into rotation ;
- there is a strong influence of laser polarization upon reactivity.

Some of these results can be explained by consideration of the potential energy surfaces in a collinear approach of the collisions. The suggested harpooning mechanism of reaction would lead to formation of a molecular switterion, Cs^+H^-.

54A

Classical and Semiclassical Theory of Fermi Resonance Between Stretching and Bending Modes in Polyatomic Molecules

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Classical and semiclassical methods are used to treat the nonlinear interaction of a Morse with a harmonic oscillator. This system serves as a model for the interaction of an excited stretching mode with a bending mode in an isolated polyatomic molecule. The expected trends in energy flow out of the excited stretching vibration are discussed using a classical resonance Hamiltonian while the semiclassical analysis provides information about the resonant zero-order state couplings.

54E

THEORETICAL STUDIES OF THE REACTION OF ATOMIC OXYGEN (^3P) WITH ACETYLENE*

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Ab initio, configuration interaction (RHF+1+2) calculations using a polarized double zeta basis set will be reported on the transition states and intermediates of the reactions,

$$O(^3P) + HCCH \rightarrow OHCCH^* \quad (1)$$

$$OHCCH^* \rightarrow H+HCCO \quad (2)$$

$$OHCCH^* \rightarrow OCCH_2 \rightarrow CH_2+CO \quad (3)$$

Addition, (1), is found to proceed on two surfaces $^3A''$ and $^3A'$ with a difference in barriers of approximately 3 kcal/mole ($^3A''$ being lower). The $^3A''$ adduct is predicted to have nearly equal barriers to hydrogen atom dissociation, (2), and hydrogen atom migration, (3), both being approximately 8 kcal/mole below the entrance channel barrier. The hydrogen migration transition state is found to be very highly nonplanar.

Since the calculations predict the exit channel barriers to be much lower than the entrance channel barrier, all of the OHCCH* formed is expected to lead to products via reactions (2) and (3), none should dissociate to reactants, (-1). Thus the total rate of reaction should be equal to the rate of addition, (1). Transition state theory calculations employing the ab initio geometries, frequencies and an adjusted barrier to addition of 2 kcal/mole lead to good agreement with numerous experimental measurements of the total rate of reaction up to 600 K. Above 1500 K, Lohr & Roth have reported separate measurements of both oxygen loss, to obtain a total rate constant, and hydrogen gain, to obtain a rate constant for reaction (2). Comparison between theory and experiment suggests that the measured total rate constant is too high and should in fact be about equal to the measured value of the rate for hydrogen production.

RRKM calculations on the branching ratio for product formation, its temperature dependence, and the lifetime of OHCCH* will also be reported. These results will be compared with available thermal and molecular beam measurements.

*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under Contract W-31-109-ENG-38.

E4C

ABSTRACT

FOR

1985 CONFERENCE ON THE DYNAMICS OF MOLECULAR COLLISIONS

Chemiluminescence of the $H^+ + F^- \dashrightarrow HF;B^1\Sigma$ Reaction

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The $H^+ + F^-$ ion-ion recombination reaction populates the $HF;B^1\Sigma$ state, which has an attractive potential curve that is free from any crossing with other states. The resultant chemiluminescence can be attributed only to the $HF;\ X^1\Sigma \leftarrow\!\!- - B^1\Sigma$ transitions. Results obtained from a fast-flow reactor with flow rate of ~80 m/sec and ~1 torr pressure will be presented and discussed. The chemical kinetics is complicated by two competing reactions. The $H^+ + F^- \dashrightarrow H(n=2) + F(^2P_{3/2})$ neutralization reaction is thermally neutral to within 0.07 kcal/mole. This translates into a electron-transfer occuring at an internuclear distance of ~4800 Å. When the hydrogen atom is in the 2p state, this reaction can be monitored via the Lyman-α line emission. But, the $\ell=0$ channel leads to the H(2s) metastable state whose detection presents problems. The other competing reaction of $H_2^+ + F^- \dashrightarrow HF(B^1\Sigma;v')$ populates $v'<33$ levels and their emission interferes with the main reaction. The presence of the H_2^+ ion in the H^+ ion source necessitates the inclusion of this three-atom exchange ion-ion recombination reaction into consideration.

55A

Abstract for contributed poster paper at the 1985 Conference

on the Dynamics of Molecular Collisions

Statistical reaction rate theory for transition states of any looseness: Application to methyl radical recombination.

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Thermal high pressure recombination rate constants for

$$2\ CH_3 \longrightarrow C_2H_6$$

have been calculated using a statistical model developed earlier[1] to describe reaction rates for systems having transition states of any looseness. Noteworthy features are the separation of "transitional" and "conserved" degrees of freedom in going from reactants to products, the accurate (classical) treatment of these transitional modes, and the use of a physically reasonable full potential energy surface for the transitional modes. The transition state location was determined variationally for each pair of (E,J) values and the resulting fluxes were then averaged over the appropriate distributions in E and J. Over the temperature range 300°-2000°K our results reproduce the experimentally determined temperature dependence of the recombination rate constant[2], in contrast to a number of different statistical models.

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55B

ENERGY DISPOSAL IN REACTIONS OF F ATOMS WITH NH_3, N_2H_4, HN_3 AND H ATOMS WITH ClO*

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Flowing-afterglow IR chemiluminescence studies of F atom reactions with NH_3, N_2H_4 and HN_3 are reported. The NH_3 reaction has been the subject of repeated studies by both arrested relaxation IR chemiluminescence techniques and contradictory results have been reported. Previously, we[1] have reported that this reaction takes place by direct abstraction mechanism with inverted HF(v) populations whereas Donaldson et. al.[2] favor a non-inverted HF(v) distribution from arrested relaxation measurements. The F + ammonia reaction is one of the reactions in which the product distribution data from two methods do not agree. The major difficulty in obtaining the primary HF(v) distribution is the vibrational relaxation by the parent molecule, as well as the contribution to HF(v) formation from the fast F atom + radical fragment secondary reaction. In the present experiments the HF(v) distributions were studied as a function of F atom and RH concentrations to eliminate (or indentify) the consequences of relaxation and secondary reactions. The possible effect of F atom precursor was also studied by using SF_6 and CF_4 as the F atom sources. The primary HF(v) distributions from NH_3, N_2H_4 and HN_3 reactions will be discussed. The secondary reactions also will be considered, but not at state-to-state level.

The H atom reactions with Cl_2O and ClO_2 were studied by IR chemiluminescence (flowing-afterglow) technique in order to investigate the secondary reaction H + ClO. The branching of the product channel into both OH and HCl has been observed, the latter being favored over the former. These results are also reported and discussed at the state-to-state level.

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55C

TRANSIENT CARS STUDIES OF AZOALKANE PHOTODISSOCIATION

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A topic of long-standing interest in physical organic chemistry is the mechanism of azoalkane dissociation. Gas phase molecules in this class, of which azomethane (CH_3-N=N-CH_3) is the simplest member, form N_2 and two alkyl radicals when excited by ultraviolet light. An important unresolved question is whether the two C-N bonds break in a sequential mechanism, forming a transient diazenyl radical intermediate, or in a synchronous process, forming all three fragments at once. We will present results obtained with direct time-resolved vibrational spectroscopy that give insight into the dissociation process.[1]

Our experimental method uses 355 nm sample excitation followed by probing with CARS spectroscopy. Excitation and probing beams are derived from sequenced Q-switched Nd:YAG-based laser systems that provide spectral and time resolutions of 0.3 cm^{-1} and 7 ns. We have measured the appearance kinetics of fragments from azomethane at the Q-branch Raman frequencies of the N_2 fundamental vibration-rotation band and the recently uncovered ν_1 band of methyl radical.[2] Both the methyl and N_2 products were found to be formed within the instrumental time resolution. Based on the kinetic data for N_2, we deduce an upper limit of 2 ns on the lifetime of any methyl diazenyl intermediate in this system.

Spectral scans at early time delays after excitation reveal the photofragments' unrelaxed internal energy contents. The nascent N_2 vibrational distribution was measured as 84% in v=0, 16% in v=1, and <3% in v>1, corresponding to a vibrational energy content of 375 cm^{-1}. We view this result as consistent with the theoretical prediction of a sequential dissociation mechanism.[3] Data will also be presented on the unrelaxed rotational temperature of the N_2, on anharmonically shifted methyl ν_1 transitions that reflect excitation in other modes, on collisional relaxation rates of the methyl vibrational energy, and on the results of similar experiments with an asymmetric azoalkane.

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56A

The State Selective Reaction Dynamics of Electronically Excited Sodium Atoms with Hydrogen Chloride and Molecular Oxygen

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The endothermic reactions:

$$Na(3^2S_{1/2}, 3^2P_{3/2}, 4^2D_{5/2}, 5^2S_{1/2}) + HCl(X^1\Sigma^+) \rightarrow NaCl + H \quad \Delta H=5.6 \text{ kcal/mole}$$

$$Na(3^2S_{1/2}, 3^2P_{3/2}, 4^2D_{5/2}, 5^2S_{1/2}) + O_2(X^3\Sigma_g^-) \rightarrow NaO + O \quad \Delta H=58. \text{ kcal/mole}$$

have been studied in a crossed molecular beams apparatus.

In the reaction of Na with HCl, the reactive cross section increased substantially with electronic energy. The Na(4D) and Na(5S) states produced NaCl with less translation energy release than the NaCl produced from the Na(3P) state. This is explained by an examination of the neutral and ionic potential surfaces with the conclusion that more than 2 eV was deposited into NaCl vibration.

In the reaction of Na with O_2, the Na(5S) and Na(3P) states did not produce NaO at collision energies up to 18 kcal/mole, even though energetically allowed to do so. The Na(4D) state produced NaO + O at center of mass collision energies higher than 16 kcal/mole, but not at 7 kcal/mole. The NaO produced was predominantly backwards scattered relative to the incoming sodium atoms in the center of mass frame of reference, implying that collinear and near collinear approach geometries are favored, and that the reaction proceeds directly with no collision complex formation. The NaO + O produced were very highly internally excited (>2 eV), and it is likely that $O(^1D)$ atoms were produced.

5GB

Gas Phase Organometallic Ion Chemistry and Spectroscopy

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Abstract

Gas phase metal cations M^+ are created in 1 torr of He in a fast flow reactor by focussing 308 nm excimer laser pulses onto a rotating metal disk. Subsequent M^+ ion-molecule reactions with small partial pressures of neutral reagents can be followed with a mass spectrometer. Our initial work involves reactions of Ti^+ and Fe^+ with the small alkanes CH_4, C_2H_6 and C_3H_8. An interesting feature is the observation of collisionally stabilized reaction intermediates. For example, the first step of the $Fe^+ + C_3H_8$ reaction branches between $FeC_2H_4^+ + CH_4$ elimination products and adduct ions of stoichiometry $FeC_3H_8^+$. We will describe inferences about reaction mechanisms drawn from our kinetics measurements. In addition, we hope to discuss the spectroscopy and photochemistry of the stabilized reaction intermediates as well as the effect of electronic excitation of the metal ion on the reactivity.

56
Cancelled

MEASUREMENT OF THE TEMPERATURE DEPENDENCE OF THE RATE CONSTANT FOR THE REACTION $D + H_2 (v = 1) \longrightarrow HD (v = 0,1) + H$

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As the simplest case of a bimolecular reaction of neutral species, even today the H_3-system serves as a model for the development of methods for a detailed theoretical description of chemical reactions. We have measured the temperature dependence of the reaction of D-atoms with vibrationally excited H_2 in a discharge flow system ($235\ K < T < 365\ K$). D atoms as well as vibrationally excited H_2-molecules were produced by microwave discharges. The D-atoms were detected by L_α-atom resonance absorption. Vibrationally excited hydrogen was detected by two different methods; Coherent Antistokes Raman Scattering (CARS) in one case, and collision induced HF-infrared fluorescence in the other.

Although the energy of only one vibrational quantum of the hydrogen molecule should be enough to surmount the barrier of the ground state reaction, a distinct activation energy, even for the reaction with vibrationally excited hydrogen was observed. Simple energy considerations suggest, that only one third of the vibrational energy can be used to surmount the barrier of the reaction.

The comparison of our results with theoretical predictions shows a qualitative agreement between theory and experiment regarding the activation energy of the reaction with H_2 ($v = 1$). On the other hand there are still big differences between theory and experiment regarding the absolute value of the rate constants.

57A

TORSIONAL VIBRATIONS IN BIARYLS

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Effective torsional potentials of the form $V = \frac{1}{2} \sum_n Vn(1-\cos n\phi)$ have been determined for a variety of biaryl molecules (e.g. 9-phenylanthracene) by simulating torsional vibrational energy level spacings measured from jet-cooled LIF spectra. The shape of the torsional potential and the equilibrium value of the torsional angle depend on steric interactions and resonance effects within the molecule. The geometries of the ground and excited states relative to each other are confirmed by comparison of calculated Franck-Condon factors with the observed intensities of the torsional progressions.

57B

The dynamics of OH production in the reactions of $O(^3P)$ with organic molecules

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The hydrogen atom abstraction reactions of $O(^3P)$ with ethanol and benzene have been studied in crossed-molecular beam experiments with laser fluorescence detection of the OH product. These are compared with other H atom abstraction reactions.

In $O(^3P)$ + ethanol, there are two possible sites for abstraction: the ethyl or hydroxyl protons. At the energy of the experiment (E_{trans} = 30 kJ mol^{-1}) a branching ratio of $\sigma(OH)/\sigma(C_2H_5) \sim 2.2$ was found. The amount of OH rotational excitation is low ($\langle F_R \rangle \sim 4\%$) and indicates that the dynamics are direct and that a collinear approach of the oxygen atom to the bond under attack is favoured. Vibrationally excited OH in v = 1 is produced ($\sigma(v = 1)/\sigma(v = 0) = 0.22$) and can only be formed by abstraction from an ethyl proton.

The endoergic production of OH(v = 0) in the reaction $O(^3P)$ + benzene has been studied at enhanced collision energies (69 kJ mol^{-1}). Again there is a low degree of OH rotational excitation indicating a collinear O—H—C transition state. A non-statistical population of the OH lambda doublet states is observed and this is rationalised in terms of a preferred orientation of the singly occupied π orbital on the OH with respect to the plane of the benzene molecule at the point at which the reaction products separate.

57C

PHOTOLYSIS OF ACETYLENE AT 193.3 NM IN A MOLECULAR BEAM

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The photolysis of acetylene at 193.3 nm has been observed in a molecular beam. The collision free processes observed at fluences as low as 10^{26} photons cm^{-2} sec^{-1} are I and II.

$$C_2H_2 \xrightarrow{193\ nm} C_2H + H \qquad \text{I}$$

$$C_2H \xrightarrow{193\ nm} C_2 + H \qquad \text{II}$$

The translational energy distribution for I peaks at about 6 kcal/mole and has a maximum release of translational energy of 16 ± 2 kcal/mole giving a C-H bond energy for ground state acetylene of 132 ± 2 kcal/mole. The bending frequency in C_2H is shown to be 550 ± 100 cm^{-1} and is strongly excited in the photolysis. The translational energy distribution for process II also peaks away from zero and is consistent with formation of $C_2(^1\pi_u, {}^1\Sigma_g^+, {}^3\pi_u)$. The experiment suggests the need for ab initio calculations on the 1'A" surface of acetylene.

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58A

ANGULAR, VELOCITY, AND EXCITED STATE DISTRIBUTIONS OF SPUTTERED ATOMS*

C. E. Young, M. J. Pellin, W. F. Calaway, and D. M. Gruen

The population of excited levels of sputtered atoms is expected to depend strongly on their component of velocity normal to the surface of origin; thus, angular, velocity, and excited state distributions are interdependent. For example, the probability for a sputtered atom to escape a surface in an electronically excited state should be enhanced at high velocity and at a direction along the surface normal.

A scanning, narrowband laser system [1] provides the means for measuring, with high resolution ($\delta v < 100$ m/s), velocity spectra of atoms sputtered in a specific quantum state. The bombarding ion beam is maintained at a fixed, near-normal angle of incidence (14°). Ejected atoms are monitored only over a narrow (4°) angular range, at an angle to the surface normal that varies from 23 to 90 degrees. The strongest effect on excitation and velocity spectra is expected for the latter case, i.e., directions of ejection such that departing atom grazes the surface.

Fluorescence detection techniques were used in measurements on pure Fe sputtered in low excitation states by 3-keV Ar^+. Early results with the apparatus included a study of the effect of the angle of ejection on the production of excitation in sputtered atoms. Population in the J=0 and J=4 components of the a^5D_J ground electronic configuration were monitored by broadband laser excitation for ejection angles between 24° and 90° to the surface normal. Population (atomic density) in the J=4 ground state was observed to be essentially independent of ejection angle over the entire range covered, while the J=0 excited state at 978 cm^{-1} exhibited significant reduction as the 90° ejection direction was approached. De-excitation of J=0 atoms which spend a relatively long time near the surface is thus indicated. A corresponding depletion of the low velocity region is thus expected in velocity resolved population studies at a fixed ejection angle. These experiments are currently in progress.

* Work performed under the auspices of the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy.

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POST-DEADLINE POSTER PAPERS LISTED BY TITLE ONLY

58B ..... Peter B. Armentrout, University of California, Berkeley, "Energy Dependence of Ion-Molecule Reactions"

58C ..... Richard J. Brudzynski, Anne-Marie Schmoltner, Sheng Yu Huang, and Yuan T. Lee, University of California, Berkeley, "Crossed Molecular Beams Study of the $O(^3P)$ + Allene Reaction"

59A ..... Laurie J. Butler, University of California, Berkeley, "Specific Photodissociation Pathways of CH_2BrI from Three Different Electronic States"

59B ..... Sally Chapman, University of Colorado, Boulder, "Collinear Heavy-Light-Heavy Dynamics in Ionic Systems"

59C ..... James Donaldson and Stephen R. Leone, University of Colorado, Boulder, "Energy Distributions in the CH_3 and CO Products of the 193 nm Excimer Laser Photolysis of $(CH_3)_2CO$"

60A ..... J. S. Binkley, Sandia Livermore Laboratory and Michael J. Redmon, Chemical Dynamics Corp., "A Potential Energy Surface Suitable for Calculations of Energy Transfer in HF-HF Collisions"

60B ..... Brian Stewart, Massachusetts Institute of Technology, Cambridge, "Inducing Quasi-Resonant V-R Energy Transfer with High Rotation and Low Velocity"

60C

Chemical reactions on a Pt(111) surface

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By using a semiclassical model for atom/molecule surface scattering has it been possible to study the reations $C + O \rightarrow CO$ and $CO + O \rightarrow CO_2$ catalyzed by a Pt(111) surface. The model includes interaction with the surface phonons through a time and temperature dependent interaction potential. Reaction probabilities and final state distributions are obtained as a function of initial kinetic energy, approach angle, surface temperature and initial internal state. Adsorption probabilities and information upon phonon excitation may also be obtained.

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1985 Conference on the Dynamics of Molecular Collisions
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